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ON THE VOLUMETRIC ESTIMATION OF ACETONE.

By Lyman F. Kebler.

Since the modern developments in the manufacture of acetone, the application of this product has been developed in many directions. As a solvent its uses appear to be almost unlimited, in both analytical and technical operations. Ethyl alcohol, wood alcohol, ether and acetic ether have been displaced by it in many instances, not only as being a more economical solvent, but a better general solvent. Prof. S. P. Sadtler[1] has proposed its use for the technical analysis of asphalt; C. Kippenberger[2] has employed it as a solvent in volumetric determinations of alkaloids by means of Wagner's reagent; and H. Trimble and J. C. Peacock[3] have used it in the preparation of tannic acid. These are only instances of the possibilities of acetone.

Now, it can reasonably be expected that the manufacture of this product will be materially cheapened in due time, and, with this cheapening, samples of various degrees of purity will be met with; then the analyst will be called on to devise ways and means for deciding in favor of the deserving products.

At present, we are not in position to determine the acetone, or dimethyl ketone, in various mixtures with accuracy. The commercial acetone generally contains bodies, besides acetone, that respond to the iodoform reaction, on which all of our analytical methods are

[1] 1895, *J. Frank. Inst.*, 140, 383.
[2] 1896, *Ztschr. anal. Chem.*, 35, 10, and 422.
[3] 1893, Am. J. Pharm., 65, 435; *Proc. Am. Pharm. Assoc.*, 41, 110.

based. The writer examined a sample of acetone that contained 6 per cent. of material (higher ketones?) that possessed a boiling point of 80° C. and above; yet it proved on analysis to contain 20 per cent. of iodoform-yielding substances by our present methods.

The specific gravity is of little value, since there are a number of products formed during the destructive distillation of the acetates that possess practically the same specific gravity as acetone. An actual case will illustrate this fact admirably. A certain make of acetone was examined, and on submitting the results of the analysis the producer protested loudly. He maintained that their product contained 98 per cent. of pure acetone according to the alcoholometer. Would methyl alcohol contain 98 per cent. of acetone if, on immersing the alcoholometer, it sank to the 98 per cent. mark? Comment is unnecessary.

The boiling point is of considerable value, but some allowance must be made even for this constant. A sample, assaying 91·96 per cent. of acetone, yielded, on distilling 100 c.c., the following fractions: from 55°–58° C. = 6 c.c.; 58°–59° C. = 20 c.c.; 59°–60° C. = 30 c.c.; 60°–62° C. = 25 c.c.; 62°–65° C. = 10 c.c.; 65°–70° C. = 3 c.c.; 70° and above = 6 c.c. Another sample, assaying 96·95 per cent. of acetone, boiled between 56° and 61° C., with a small amount of residue.

A word about the stability of acetone at this point may not be inappropriate. On assaying a drum of acetone, it was found considerably below the requirements. On informing the manufacturer concerning it, he made the assertion that acetone deteriorated very materially in a month. This information was quite contrary to the writer's experience. For example, a sample of acetone had been kept by the writer for two years, about one-half of the time in a dark, dry cellar, in an ordinary greenish, cork-stopped, glass bottle; the remainder of the time the bottle and contents were kept in direct and diffused sunlight. This acetone assayed 97·12 per cent. This product certainly did not deteriorate much in these two years; for the best commercial acetone obtainable contains only from 97 to 98 per cent. of pure acetone. Dr. Squibb, in a private communication, writes thus on this point: "Nothing within our knowledge or experience has ever led us to suspect any spontaneous change in acetone by keeping, and I do not believe there is any such change either in full or partly filled vessels."

A. Lieben,[1] in 1870, discovered that certain organic groups, such as CH_3, COC —, CH_3 CH(OH)C —, CH_3CH_2OH, etc., when treated with iodine in the presence of an alkali, yield iodoform. Iodoform itself, however, was discovered in 1822, by Serullas.[2] With some of the groups the application of heat is necessary to bring about the reaction. Lieben also observed that methyl alcohol did not respond to this test, and suggested at the same time that this fact might be of service in establishing the purity of this alcohol.

Ten years later, G. Kramer[3] devised a gravimetric process, based on the iodoform reaction for estimating acetone in wood alcohol. The results obtained by this method were rarely concordant, consequently it was unsatisfactory.

From 1884 to 1888 much interest was manifested in this country concerning the manufacture of chloroform from acetone. During this period, W. R. Orndorff[4] and H. Jessel studied the action of chlorinated lime on acetone in the manufacture of chloroform. On the results of this investigation J. Messinger[5] based the first volumetric method for estimating acetone in wood alcohol. The method has been applied with success to all[6] mixtures in which acetone generally occurs.

The reactions[7] involved for this volumetric process are as follows:

$$I_2 + 2KOH = KIO + KI + H_2O.$$
$$CH_3COCH_3 + 6KIO = CH_3COCI_3 + 3KOH + 3KI.$$
$$CH_3COCI_3 + KOH = CHI_3 + KC_2H_3O_2.$$
$$KIO + KI + 2HCl = I_2 + 2KCl + H_2O.$$
$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O.$$

The solutions required for the process are as follows: 56 grammes of potassium hydroxide, free from nitrite, dissolved in distilled water and made up to 1 litre.

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[1] 1876, *Ann.* (Liebig) *Supp.*, 7, 218 and 377.

[2] 1822, *Ann. chem. phys.*, 20, 165.

[3] 1880, *Ber. d. chem. Ges.*, 13, 1000; *Ztschr. anal. Chem.*, 19, 498.

[4] 1888, *Am. Chem. J.*, 10, 363.

[5] 1888, *Ber. d. chem. Ges.*, 3366.

[6] See literature at the end of the article.

[7] There may be some question concerning the actual reactions, but the basis of calculation is not involved. Krämer expresses it in a single equation: $CH_3COCH_3 + 6I + 4KOH = CHI_3 + 3KI + KC_2H_3O_2 + 3H_2O$.

Solution of hydrochloric acid, specific gravity 1·025.

A decinormal solution of sodium thiosulphate.

A starch solution.

A dilute solution of acetone containing from 1 to 1½ per cent. of acetone by weight. This is prepared from the acetone or acetone solution to be examined. The writer prepares this by weighing the acetone in a beaker containing water, transferring to a graduated cylinder, rinsing the beaker well with water and making up to a definite volume.

Having prepared the above solutions, place from 25 to 30 c.c. of the potassium hydroxide solution into a suitable flask, add 1 or 2 c.c. of the diluted acetone solution, *very carefully* measured, or if greater accuracy is desired, carefully weigh the aqueous acetone, mix well, and run in from a burette, while rotating the flask, from 25 to 30 c.c. of the iodine solution; insert the stopple quickly and agitate vigorously for one minute. After shaking, render the mixture acid by means of the hydrochloric acid solution; add, while rotating, an excess of the sodium thiosulphate solution. Allow the mixture to stand several minutes, add the starch indicator, and re-titrate the excess of the sodium thiosulphate with the iodine solution. From the above data the per cent. of acetone can readily be calculated; thus 1 molecule of acetone (58) requires 3 molecules of iodine (762) to form 1 molecule of iodoform. Expressing it in the form of a proportion, letting y equal the amount of combined iodine, and x equal the amount of acetone, we have;

$$762 : 58 :: y : x \quad \text{or } x = y.\ \frac{58}{762} \text{ or } x = y.\ 0{\cdot}07612.$$

Before leaving the process, it may be well to direct attention to several important points. After adding the iodine solution, agitation must not be delayed if concordant results are desired, since the active agent KIO is rapidly converted into KI and KIO_3. Experiments have proven that it becomes inactive in one-half an hour. It is essential to allow the mixture to stand a few minutes after adding the sodium thiosulphate solution, in that the reaction is not immediate. It is necessary to add an excess of the iodine and sodium thiosulphate solution, respectively, at the time of adding them, in order to secure completed reactions.

MM. F. Robineau[1] and G. Rollin, in 1893, proposed another volumetric method for estimating acetone. This method was first brought to the writer's notice through the generosity of Dr. Squibb and the kindness of his chemist, Dr. L. L. Jackson, while visiting the laboratory of the former last summer. Prior to this time Messinger's process had been used exclusively by the writer. R. and R.'s method is applied by mixing an aqueous acetone solution with a strongly alkaline solution of potassium iodide and converting the acetone into iodoform by means of a titrated solution of sodium hypochlorite, the end reaction being determined by means of a bicarbonated starch solution.

The writer has not applied the above process to any extent, but has studied and worked with Dr. Squibb's[2] modification of the same considerably.

The solutions required for this modification and the methods of preparing them are as follows:

Pure acetone made by the bisulphite process.

An alkaline solution of potassium iodide. Dissolve 250 grammes of pure potassium iodide in distilled water and make up to 1 litre. Dissolve 257 grammes of sodium hydroxide, purified by alcohol, in distilled water and make up to 1 litre. Allow the insoluble part to subside and mix 850 c.c. of the clear solution with the litre of potassium iodide.

Solution of hypochlorite, containing about $2\frac{6}{10}$ per cent. of available chlorine. To each litre add 25 c.c. of sodium hydroxide solution, specific gravity 1·29.

Bicarbonated starch solution. Treat 0·125 gramme of starch with 5 c.c. of cold water, then add 20 c.c. of boiling water and boil a few minutes, cool and add 2 grammes of sodium bicarbonate. The keeping quality of this solution is certainly an agreeable surprise. A sample prepared four months ago is as delicate to-day as a freshly prepared one.

The manner of application. Prepare an aqueous solution of the pure acetone of such a strength that each 10 c.c. contains exactly $\frac{1}{10}$ gramme of the acetone. Of this solution, accurately measure,

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[1] 1893, *Moniteur Scientifique* (4), 7, pt. 1, 272; translation in *J. Am. Chem. Soc.*, 18, 1068.

[2] 1896, *J. Am. Chem. Soc.*, 18, 1068.

with a pipette, 10 c.c. into a 50 c.c. beaker, add 20 c.c. of the alkaline potassium iodide solution and mix well. To this mixture add, from a burette, while vigorously agitating the contents of the beaker, the standard solution of sodium hypochlorite in rapid drops until about 9 c.c. have been run in. Allow the iodoform to subside, which it does rapidly, then add a drop or two of the hypochlorite solution; should a cloudiness result, add another ½ c.c. of the hypochlorite solution; agitate well; allow the iodoform to subside, etc., until just a faint turbidity results on adding the hypochlorite solution. Now agitate the solution well; transfer a small drop to a white porcelain tile; in a similar manner, bring a drop of the bicarbonated starch solution near this drop, then connect the two drops by means of a glass rod. If a blue color does not develop at the point of union, not enough of the hypochlorite solution has been added. Continue adding the hypochlorite solution, a small quantity at a time, agitating and testing, until a blue line is just formed at the meeting of a drop of the starch solution and a drop of the mixture titrated. Ordinary starch solution is valueless for this end reaction.

The number of c.c. of the hypochlorite solution required to complete the reaction is the amount of this active agent needed to convert $\frac{1}{10}$ gramme of acetone into iodoform. From this basis calculations for any amount of acetone are readily made.

In estimating the amount of acetone in any solution, first prepare an aqueous solution containing from 1 to 2 per cent. of acetone by weight, then proceed as above for establishing the standard with pure acetone. For fuller details the reader is referred to the original communication.

The two latter methods will meet with two objections: first, a *pure acetone*, and second, the tedious, time-consuming drop end reaction. Pure acetone is not so readily prepared. It necessitates the preparation of an acetone absolutely free from other ketones, before the bisulphite process can be applied. The writer has not been able to secure acetone that assayed more than 99·73 per cent. of pure acetone by either Messinger's process or the one presently to be described. This small quantity may have volatilized, but the loss would be practically constant for all the methods, consequently, the basis of calculation for the pure acetone methods would be 100, when in reality it is less. The difference may again be due to some

slight inaccuracies in the volumetric solutions. Grant that absolutely pure acetone is made, it is not readily secured when desired.

The writer has adapted Dr. Squibb's modification so that both the pure acetone and the drop end reaction are eliminated. In this process the following solutions are employed:

A 6 per cent. solution of hydrochloric acid.

The alkaline solution of potassium iodide of Dr. Squibb.

A decinormal solution of sodium thiosulphate.

Sodium hypochlorite solution, about $\frac{1}{5}$ normal, or containing from $2\frac{6}{10}$ to 3 per cent. of available chlorine. To prepare this solution, intimately mix 100 grammes of bleaching powder (35 per cent.) in 400 c.c. of distilled water. Dissolve 120 grammes of crystallized sodium carbonate in 400 c.c. of hot distilled water, and immediately pour the latter into the former. Cover the vessel and allow to cool, then decant the clear liquid, filter the remainder and to the filter add enough water to make up to 1 litre. To each litre add 25 c.c. of sodium hydroxide solution, specific gravity 1·29.

An aqueous solution of acetone containing from 1 to 2 per cent. by weight. Prepared as for Messinger's process above. To estimate the acetone, place 20 c. c. of the alkaline potassium iodide solution into a suitable flask add 10 c.c. of the diluted aqueous acetone solution, or weigh if greater accuracy is desired; mix well, and run in from a burette, while rotating the flask, an excess of the sodium hypochlorite solution, insert the stopple quickly and shake well for one minute. After agitating, render the mixture acid by means of the hydrochloric acid solution, add, while rotating the flask, an excess of the sodium thiosulphate solution, and allow the mixture to stand a few minutes. Then add the starch indicator and re-titrate the excess of the sodium thiosulphate.

The relation of the sodium hypochlorite solution to the sodium thiosulphate solution being known, the percentage of acetone can readily be calculated from the above data. One atom of available chlorine will liberate 1 atom of iodine from the potassium iodide of the alkaline solution, or 1 c.c. will liberate just enough iodine to make 1 c.c. of iodine solution of the same normal strength as the sodium hypochlorite solution originally was; therefore, by reading the number of c.c. of sodium hypochlorite solution consumed as so many c.c. of iodine solution of the same normal strength, we reduce the calculation to the basis of iodine. For explanation from here see Messinger's process above.

Example of calculation. Ten c.c. of the acetone solution, containing 1 gramme of the solution to be analysed, required 14·57 c.c. of N × 0·806 sodium hypochlorite solution, which formed 14·57 c.c. of iodine solution of the same strength; or combining we have:

$$\frac{14{\cdot}57 \times 0{\cdot}806 \times 0{\cdot}1265 \times 0{\cdot}07612}{1 \text{ gramme of solution.}} = \text{amount of acetone} =$$

11·307 per cent.

On comparing Messinger's, Dr. Squibbs' and the writer's adaptation with the same solution, the following results, in per cent. were obtained:

	Messinger.	Squibb.	Author.
Pure acetone	99·69	99·95	99·73
Residue 80° C. and above .	20·00	19·67	20·39
Purified by fraction . . .	99·03	99·00	99·41
Commercial acetone . . .	96·23	96·00	96·63
" " . . .	98·00	97·83	97·93
" " . . .	94·30	94·00	94·46
" " . . .	94·80	94·70	94·81
" " . . .	97·12	96·23	96·42
" " . . .	94·93	94·80	94·39
" " . . .	96·88	96·56	96·79
" " . . .	97·32	97·28	97·45
" " . . .	90·74	89·03	90·51
" " . . .	98·82	96·11	98·62
" " . . .	92·32	92·20	92·94
Wood alcohol	14·61	14·49	14·78
" "	11·81	11·73	12·00
Crude wood alcohol . . .	11·23	11·00	11·42

The above table clearly shows that the results obtained by Dr. Squibb's process are a trifle too low, notwithstanding the fact that its basis of calculation gives it some advantage. The method is represented to yield satisfactory results for ordinary work, and that it certainly does. The difficulty with this method lies in the end reaction. According to some experiments made by the writer, it is necessary to have present a larger excess of the active agent, to bring about the completed reaction, than the end reaction allows.

The iodoform reaction with ethyl alcohol is an endothermic one, consequently its presence does not interfere with the estimation of acetone, which does not require the presence of external heat to bring about the reaction. The same holds true for all other groups of endothermic reaction.

LITERATURE NOT IN THE BODY OF THE ARTICLE.

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1890, Fr. Collischonn, "Ueber die gebräuchlichen Methoden zur quantitativen Bestimmung des Acetons," *Ztschr. anal. Chem.*, 29, 562.

1890, H. Huburt, "Zur quantitativen Bestimmung des Acetons im Harn," *Ztschr. anal. Chem.*, 29, 632, from Neubauer und Vogel; "Anleitung zur Analyse des Harns," 9 Auf., 471.

1890, L. Vignon, "Dosage de l'acétone dans l'alcool méthylique et dans les méthylènes de dénaturation," *Comp. rend.*, 110, 534.

1890, G. Arachequesne, "Dosage de l'acétone par l'iodoforme," *Comp. rend.*, 110, 642; *Ztschr. anal. Chem.*, 27, 695.

1894, N. Savelieff, "Ueber das Vorkommen von Aceton im Mageninhalt bei Erkrankung en des Magens;" *Berliner klin. Wochenschrift*, No. 33; und *Maly's Jahresberichte über die Fortschritte der Thierchemie*, 24, 352; 1896, *Ztschr. anal. Chem.*, 35, 507.

1896, Chr. Geelmnyden, "Ueber die Messinger'sche Methode zur Bestimmung des Acetons," *Ztschr. anal. Chem.*, 35, 503.

1896, M. Klar, "Zur Bestimmung des Acetons in Denaturirungs-Holzgeist und Rohaceton," *Die chem. Ind.*, 19, 73; *Ztschr. anal. Chem.*, 37, 595.

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TERPIN HYDRATE.

BY EDWARD T. HAHN.

In 1840, A. Wiggers contributed an article to the *Annalen der Chemie*, **33**, 358, on the crystalline substance from turpentine oil, to which, however, he applied the name *turpentine camphor*. He employed a mixture of nitric acid, alcohol and turpentine oil, and in 1846[1] (*Annalen der Chemie*, **57**, 247) reported a formula for making the substance on a large scale, stating that it could only be obtained from that variety of turpentine which yielded a crystalline compound with hydrochloric acid.

The method suggested by Wiggers was tried with commercial oil of turpentine, but it failed to produce any crystalline compound. Knowing that the oil of turpentine found on the market at the present time is occasionally adulterated with some of the heavier petroleum oils, a quantity of the commercial oil was procured and distilled with lime and water. An oil having a specific gravity of

[1] AM. JOUR. PHARM., 12, 286.

0·856, and a boiling point of from 154° to 157° C., was obtained, and this product was used in all my experiments.

The first method tried was one suggested by Carl Hempel (*Annalen der Chemie*, **153**, 71), using the following quantities:

(1) Oil of turpentine	120 c.c.
(2) Alcohol (sp. gr., 0·816)	30 "
(3) Nitric acid (sp. gr., 1·35)	30 "

These liquids were mixed in a flask in the order indicated by the numbers, and allowed to stand three days, shaking occasionally. The mixture separated into two layers, the lower one becoming quite dark in color. On the third day it was poured into a flat dish and 15 c.c. of alcohol added, and allowed to stand in a room having a temperature of about 18° C.

Crystals began to form within five days, and at the end of two weeks they had separated from the mother liquor. About 13 grammes of crystals were thus obtained. This product was purified by recrystallization in a solution of boiling alcohol, and yielded 8 grammes of terpin hydrate, which was found to answer all the U.S.P. requirements.

The mother liquor was allowed to stand for a short time, and another crop of crystals was obtained; but these, when tested with sulphuric acid, did not give the characteristic deep orange color, but a light, pinkish one, which quickly faded.

The next method tried was one suggested by Wm. A. Tilden (*Jour. Chem. Soc. Lond.*, **33**, 247), the following being the proportions of liquids used:

Oil of turpentine	60 c.c.
Alcohol	30 "
Nitric acid (sp. gr., 1·40)	60 "

In this method and all others suggested by Tilden, nitric acid having the specific gravity of 1·40 was employed, but the writer's experience with acid of this strength was that a thick resinous-like mass was obtained, which showed no signs of crystallization.

A method was also given by F. Flawitzky (*Jour. Chem. Soc. Lond.*, **38**, 264), in which he used sulphuric instead of nitric acid, and obtained a compound having the formula $C_{10}H_{18}O$.

As ethyl alcohol commands a comparatively high price at the present time, methyl alcohol was substituted for it, and the following formula was found to be very satisfactory:

(1) Oil of turpentine	120 c.c.
(2) Methyl alcohol (sp. gr., 0·801)	30 "
(3) Nitric acid (sp. gr., 1·35)	30 "

These liquids were mixed in the order indicated and allowed to stand in a flask three days and then poured into a flat dish. Taking advantage of the very slight solubility of terpin hydrate in water, 30 c.c. of this liquid were added to the mixture, with the result that the crystals separated in a much shorter time than they did with the methods previously employed. No additional crystals were formed on allowing the mixture to stand several days. The weight of the crystals obtained was 7·32 grammes, and these, on purifying from hot solution of methyl alcohol, yielded 3·2 grammes of terpin hydrate, which answered to all the tests for the U.S.P. compound.

By further evaporation an additional quantity of crystals may be obtained.

The crystals obtained by the use of methyl alcohol had a closer resemblance to the article which is found in the market, and also a more aromatic odor than those obtained by the employment of ethyl alcohol.

Amyl alcohol likewise may be used in making terpin hydrate.

An explosion occurred a few years ago (*Proc. Am. Pharm. Assoc.*, 1887) in a Parisian laboratory during the manufacture of terpin hydrate. The following proportions of liquids were employed:

Oil of turpentine	72 L.
Alcohol	50 "
Nitric acid	17 Kg.

The mixture was usually cooled in stone jars set in water, but as these were all in use at the time, a part of the mixture was poured into a wooden cask, to cool off, and as the wood did not conduct the heat away rapidly enough, a violent explosion took place, doing much damage.

Indian podophyllum, according to W. R. Dunstan (*Imp. Inst. Jour.*, December, 1896), is derived from Podophyllum emodi, and contains two to three times as much resin as the American podophyllum from P. peltatum. Dr. Mackenzie finds that the two resins (Indian and American) are identical in their medicinal-effects, and that there is no reason why the resin obtained from the Indian drug should not be substituted for the American resin.

SOLANUM CAROLINENSE.

By Charlton G. Johnson, Ph.G.

(Abstract from Thesis.)

Since its introduction to the medical profession by Dr. J. L. Napier, in 1889, several contributions to the chemistry of Solanum

Fig. 1 represents a portion of a branch of Solanum Carolinense. It shows the spiny stem, bearing the rather irregularly shaped leaves, with the small axillary leaves and the racemose flowers.

Carolinense have appeared in this Journal. In the meantime pharmacists have become better acquainted with the botany of this plant.

The microscopical characters, however, have not been so fully investigated. But, at the beginning of this article, the author wishes to call attention to a slight difference which was observed in the fruit (or berry, as it is called), obtained from two sections of the country. In the specimens obtained from the South, mainly Georgia and Florida, the calyx, though adherent, was recurved, while the berries gathered near Philadelphia had the calyx adhering to the fruit.

A transverse section of the root (*Fig. 4*) shows it to have a concentric structure caused by irregular, alternating zones of wood-

Fig. 2 shows a small portion of a branch bearing the fruit. Natural size. The berries frequently grow much larger.

parenchyma and vascular tissues. The cork tissue replacing the epidermis is composed of about three layers of cells, with the rough fissured remains of older cork cells exterior. The cork meristem in the root, as well as in the stem, shows quite plainly. The parenchyma cells of the cortex are larger in the middle bark than near the epidermis, becoming very much smaller and elongated longitudinally near the cambium zone, while in the outer and inner portions of the cortex they are, from mutual pressure, much distorted and elongated tangentially. The ducts of the xylem are large and

numerous; and seen in longitudinal-radial section (*Fig. 5*), they prove to be pitted, the pits showing an elliptical marking within a larger circular one. Spiral, annulate and reticulate ducts are also

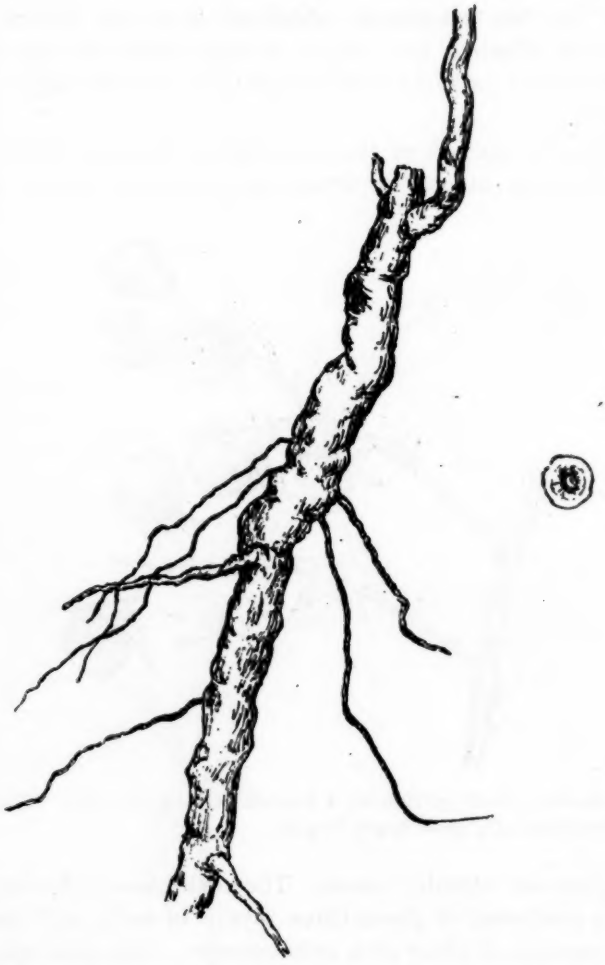

Fig. 3 is a drawing of the root of Solanum Carolinense in the fresh state. It shows the natural size of the root when about two years old.

present. The libriform cells show markings from the pressure of adjacent cells, and are usually forked at one end. In the portions of the wood studied no collenchyma was found and bast-fibres were

also absent. The medullary rays are distinct and slightly undulate, the number of rows varying from two to five or six.

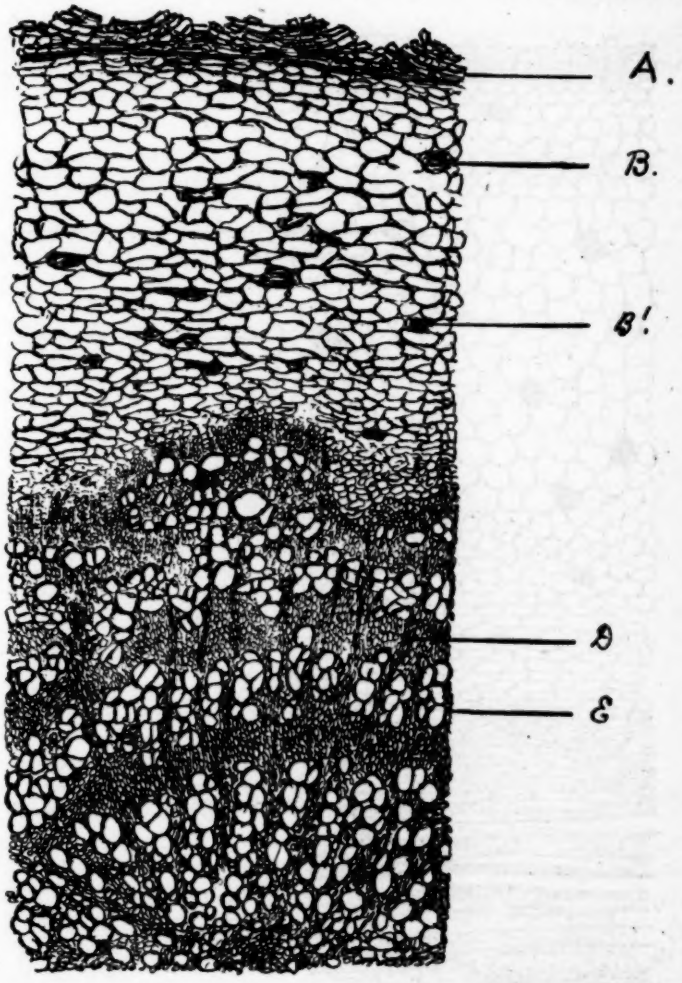

Fig. 4, portion of a transverse section of a root of Solanum Carolinense, magnified 45 diameters. *A*, ruptured cork tissue; *b* and *b'*, secretion cells containing calcium oxalate; *c*, cambium zone; *d*, medullary ray; *e*, one of the concentric layers of ducts, alternating with wood parenchyma.

The underground stem (*Fig. 6*) shows the pericycle relatively thicker and the cortex thinner than in the root. The cork tissue

resembles that of the root, except that a part of the epidermis is present. Collenchyma is found in the younger parts of the stem, though absent from the older portions. No bast-fibres were found.

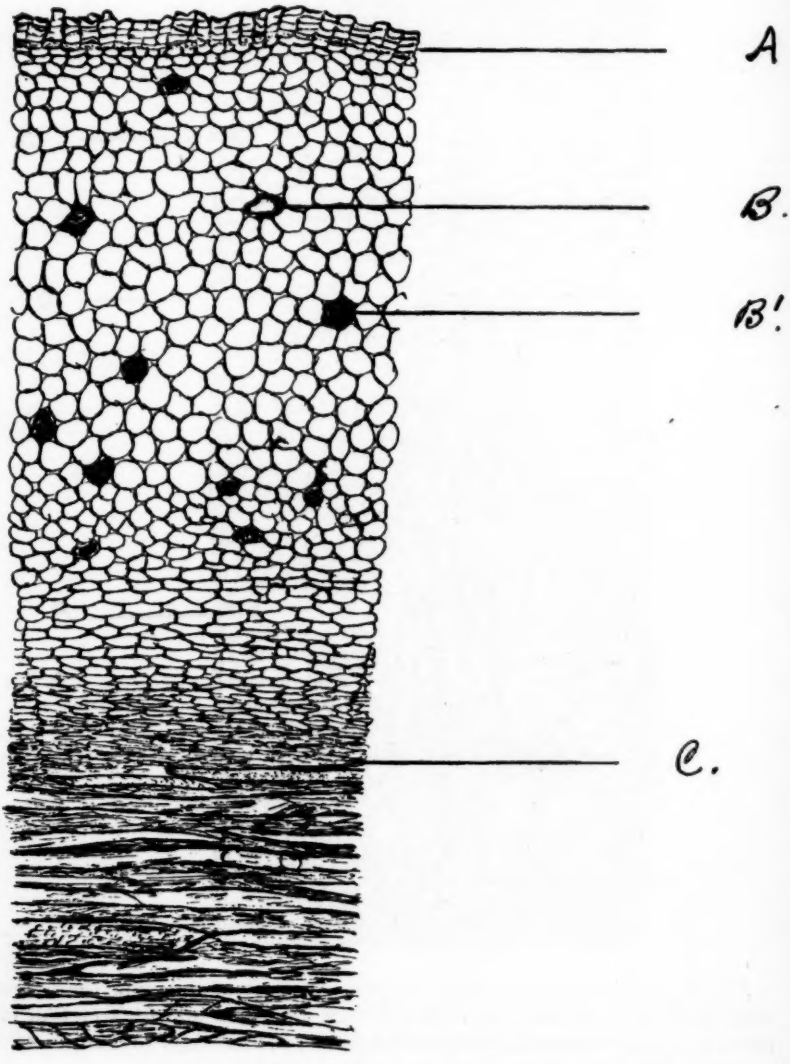

Fig. 5, longitudinal-radial section, made from a young root of Solanum Carolinense having a thick cortex, magnified 35 diameters. *A*, cork tissue; *b*, *b'*, secretion cells of calcium oxalate; *c*, the cambium, with the ducts of the xylem on one side and the phloem tissue on the other.

The cortex is mainly composed of parenchyma tissue; the cells are round, but otherwise correspond to the same tissue in the root. The woody tissue is rather irregular in width, and beside the phloem tissue on its exterior, there is a distinct inner phloem, which, though narrower in some places than in others, is distinctly discernible. The pith is composed of large parenchyma cells.

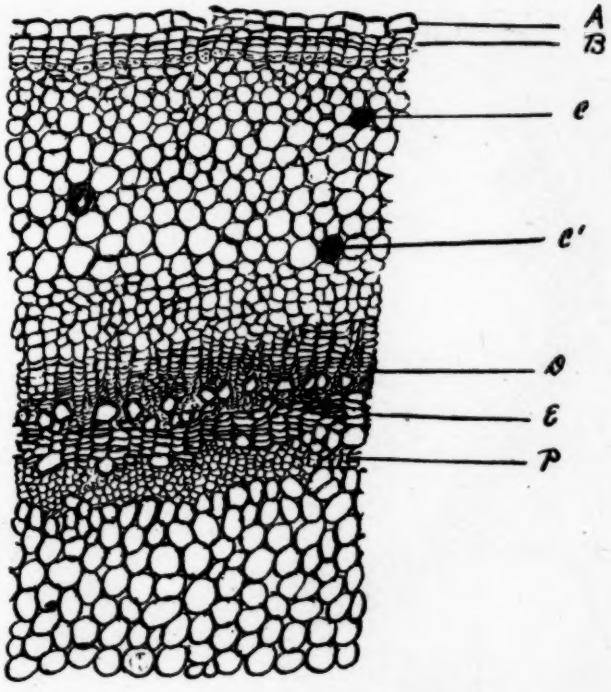

Fig. 6, transverse section of underground stem of Solanum Carolinense (from a portion just at or beneath the ground), magnified 56 diameters. *A*, epidermis; *b*, cork cells; *c*, *c'*, secretion cells of the cortex; *d*, cambium; *e*, xylem; *p*, secondary or inner phloem, beneath which are the soft, parenchymatous cells of the pith.

The petiole, as seen in transverse section in *Fig. 7*, shows three bi-collateral bundles. Beneath the epidermal tissue are several rows of collenchyma cells, and next to these are the parenchyma cells surrounding the vasal bundles. Two large secretion reservoirs are found, one on each side, near the upper surface. Some starch is present in the parenchymatous cells of the stem, principally in the

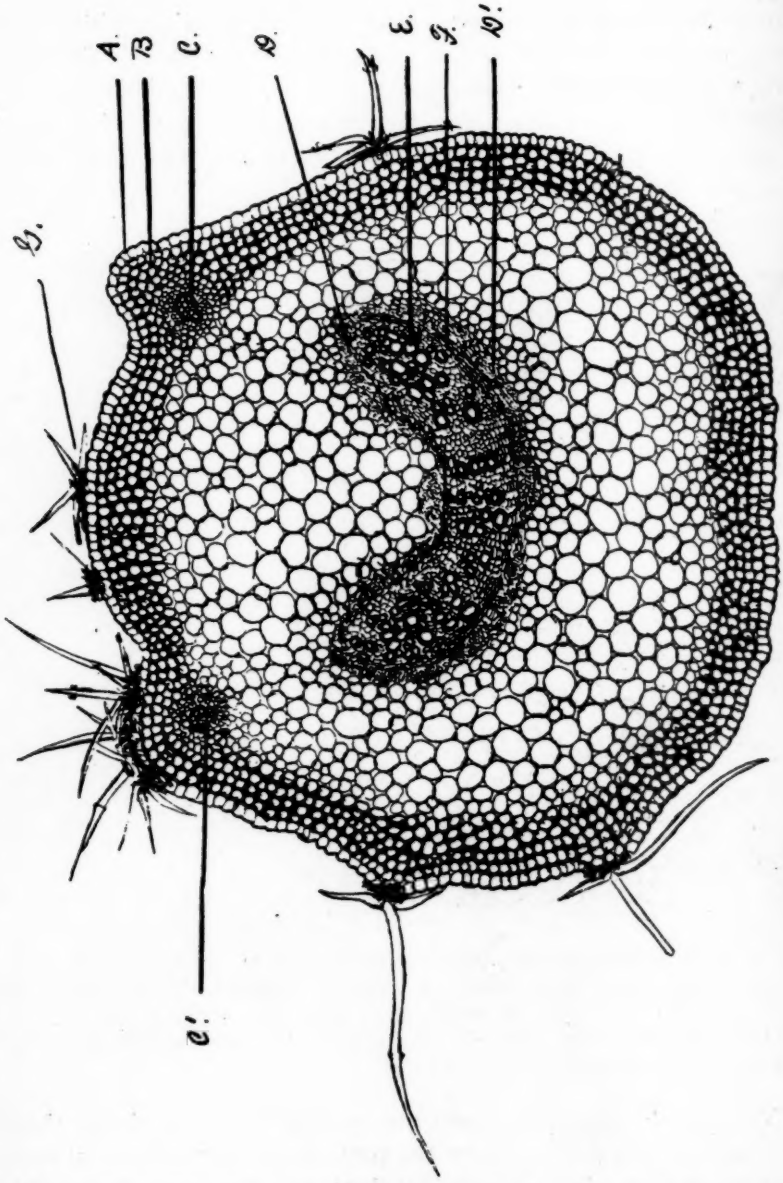

Fig. 7, transverse section of a younger portion of a petiole of Solanum Carolinense. Magnification, 65 diameters. *a*, epidermis; *b*, collenchyma tissue; *c*, *c'*, large secretion reservoirs; *d*, *d'*, upper and lower phloem tissues, respectively; *e*, xylem; *f*, meristem, found only on the lower side; *g*, stellate hair.

cortex, but it is more especially found in the cortical tissue of the root, chiefly near the pericycle. In some of the specimens examined, the whole of the cortex seemed filled with starch granules, while others failed to show its presence so profusely. The grains

Fig. 8, starch grains found in the root of Solanum Carolinense; magnified about 400 diameters.

show distinct stratification lines. In shape some were oblong, some ellipsoidal and others in clusters of two, three or four, the oval or oblong-ovate being, however, the most common form. The hilum is distinct, eccentric, and usually presents a fissured appearance.

Some of the grains were bi-nucleated and others possessed a peculiar, contorted shape. The starch grains resemble somewhat in shape those of another plant of the same genus, Solanum tuberosum, the potato. Scattered irregularly through the cortex of the root, and less profusely in the stem, are secretion cells containing a peculiar, mucilaginous-like matter. On treating these cells with potassium hydrate test solution they were rendered clear, and their contents now shown to be a white, granular or crystalline substance. This substance, by dissolving in warm hydrochloric acid, without effervescence, proved to be calcium oxalate. The tests for tannin failed to show its presence. On testing for resins and oils, with alcannin solution, small quantities of these substances were found in some of the starch-bearing cells and also in some of the lignified tissues.

In conclusion, the author wishes to express his thanks to Messrs. Parke, Davis & Co. for specimens kindly furnished, and to Dr. M. V. Ball for his valuable assistance in the microscopical work.

SOLANUM CAROLINENSE.

By M. Clayton Thrush, Ph.G.

(Abstract from Thesis.)

The author found the fruit to contain the largest amount of alkaloidal constituents; consequently, it is the most active therapeutically. The leaves came next in strength, then the root, and finally the stem, which is the least active.

In order to study the drug microscopically, sections were cut by means of the microtome from specimens of the plant which had been preserved in strong alcohol. They were then placed in Labarraque's solution until properly bleached, except those intended for the tests for tannin and oleoresin. They were then treated as follows: For double staining some of the sections were treated with iodine green, then washed to separate excess, then passed through dilute, strong and finally absolute alcohol, to anhydrate them. They were then treated with eosin, oil of cloves, and from that through pure oil of cloves, and mounted in xylol balsam. The others, after being treated with the reagent, were washed to separate excess, anhydrated by absolute alcohol and mounted in xylol

balsam. The sections which were tested for tannin and oleoresin were treated direct with ferric chloride in absolute alcohol and alcannin, respectively, then mounted in xylol balsam. These latter tests were confirmed by treating dry sections with ammonio-

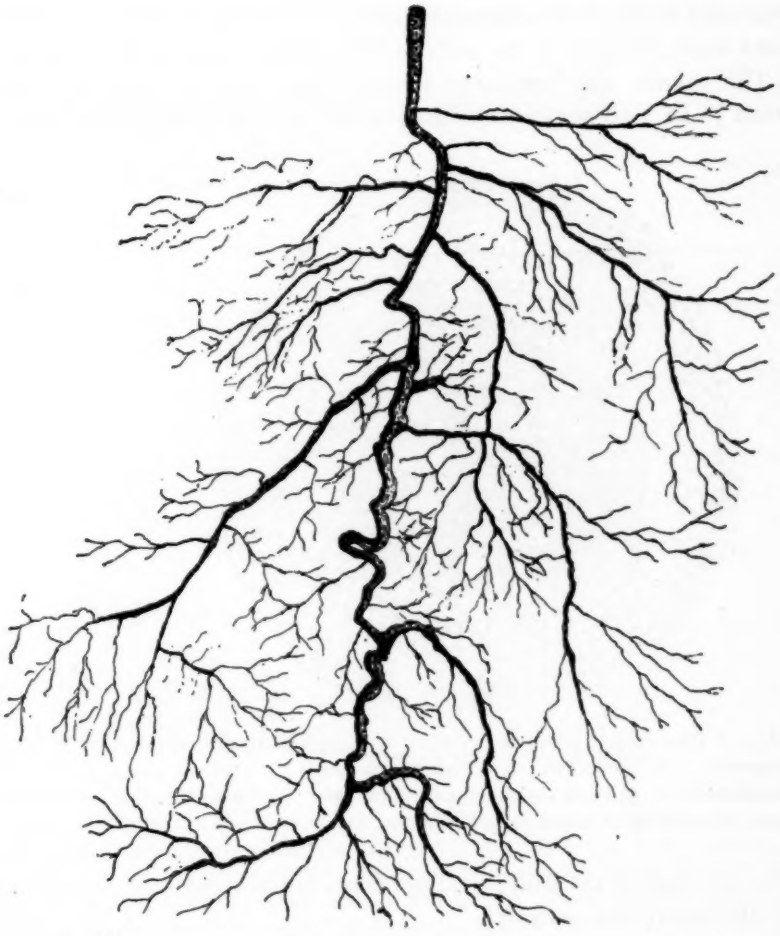

Fig. 1, underground portion of the plant, one-half natural size.

ferric alum. By treating dry sections of the young root for tannin with ferric chloride in absolute alcohol, tannin precipitates were produced in the central parenchyma and the cortical parenchyma. In the old root tannin precipitates were produced in

a great number of the cells of the cortical parenchyma, also in a few cells of the phloem tissue and the medullary rays. In the mature stem, indications of tannin were obtained in abundance, in the pith parenchyma, medullary rays, cambium zone, phloem, cortical parenchyma and suberous tissue. In the leaf indications were produced in all of the different tissues. In the fruit tannin indications were obtained in the cells of the section irregularly scattered.

The tannin was estimated by the "hide powder method," and found to be 3·10 per cent. in the leaves; 2·27 per cent. in the root;

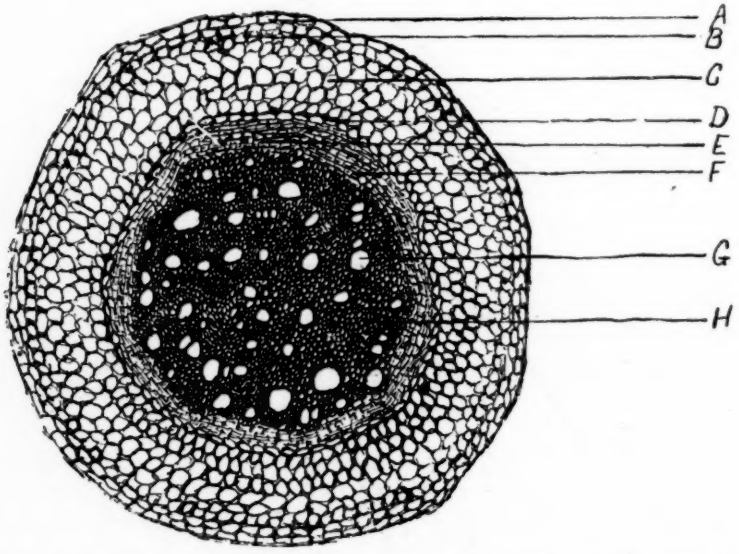

Fig. 2, transverse section of rootlet of Solanum Carolinense, magnified 75 diameters. *A*, epidermis; *b*, collenchyma tissue; *c*, cortical parenchyma; *d*, endodermis; *e*, phloem tissue; *f*, cambium zone; *g*, duct of xylem; *h*, xylem tissue, consisting of wood cells and ducts.

8·06 per cent. in the fruit; 5·06 per cent. in the stem—all calculated for absolutely dry material.

Fig. 1 represents the underground portion of the plant.

Root.—Phloroglucin and hydrochloric acid stain the xylem tissue, which is strongly lignified, a bright red. In the young undeveloped root central parenchyma exists, but as the root becomes older the xylem of the radial bundle extends to the centre with the development of rings of growth, medullary rays and a cambium zone, and

has a similar appearance to the structure of a dicotyl stem. Zinc chloriodide iodine shows an abundance of starch in the cells of the medullary rays, phloem, collenchyma and cortical parenchyma. Chloral hydrate iodine gives the same indications. The epidermis of the mature root consists of several rows of suberous tissue, which exfoliates at the surface; beneath this is a circle consisting of

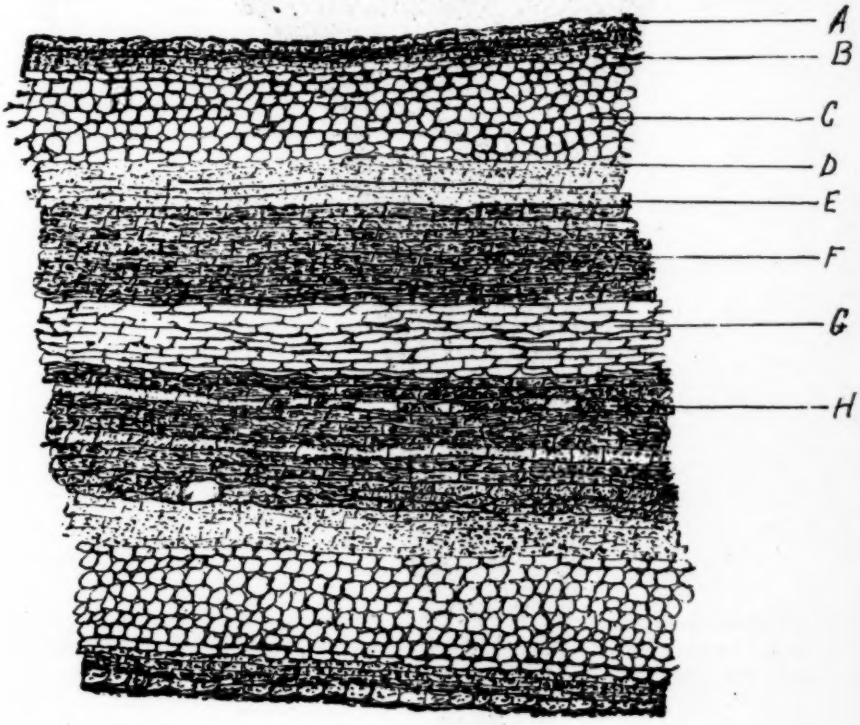

Fig. 3, longitudinal section of young root of Solanum Carolinense, magnified 75 diameters. *A*, epidermis, not yet displaced by cork cells forming beneath; *c*, cortical parenchyma; *d*, phloem tissue; *e*, cambium zone; *f*, xylem tissue, consisting of wood cells and ducts; *g*, central parenchyma, not yet developed into xylem tissue; *h*, duct of xylem.

several rows of collenchyma tissue; interior to this a layer of cortical parenchyma, consisting of several tiers of cells, then the phloem tissue and finally the xylem, which extends to the centre and is separated from the phloem by the cambium zone. The different rays are separated by the medullary rays.

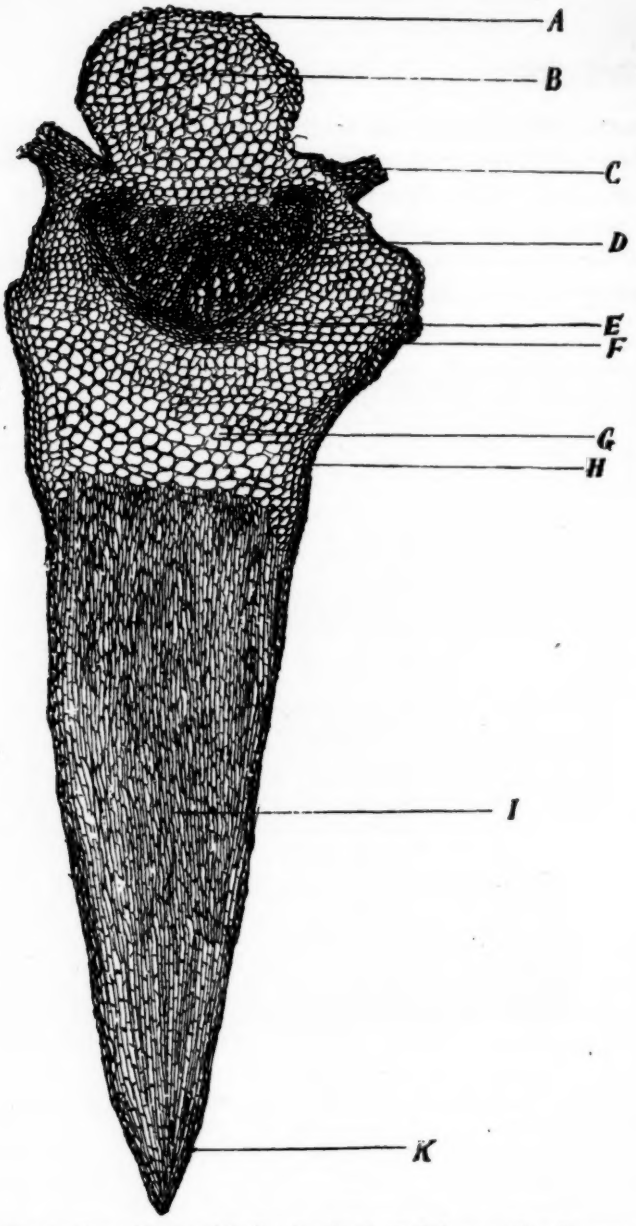

Fig. 4, transverse section of the mid-rib of a leaf of Solanum Carolinense, with one of the prickles, which is shown in longitudinal section, attached; magnification, 150 diameters. *A*, epidermal cells; *b*, parenchyma of upper portion of mid-rib; *c*, a portion of the lamina of the leaf; *d*, xylem tissue of mid-rib; *e*, cambium zone; *f*, phloem tissue of mid-rib; *g*, parenchyma of lower portion of mid-rib; *h*, collenchyma tissue; *i*, slightly lignified tissue of the prickle, which occurred on the mid-rib and was cut through longitudinally; *k*, epidermal tissue, more lignified.

Stem.—Zinc chloriodide iodine shows starch in the central parenchyma, in the cells of the medullary rays, in the cortical parenchyma, and in the cambium zone. Chloral hydrate iodine gives the same results, as does also potassium iodide iodine, but much more prominently, especially in the central parenchyma tissue, which contains an abundance of the substance. Phloroglucin and hydrochloric acid stain the xylem tissue, which is strongly lignified, a

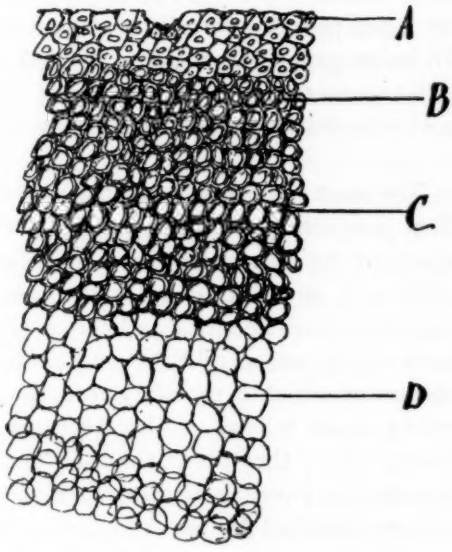

Fig. 5, portion of transverse section of fruit of Solanum Carolinense, showing the succulent tissues, magnified 200 diameters. *A*, epidermal tissue; *b* and *c*, succulent tissues, farther interior; *d*, parenchyma tissue, adjacent to the placenta.

bright red. The stem possesses open collateral bundles, which are in wedge-shaped rays, and which are separated from one an other by medullary rays. In the mature stem the outer portion of the section consists of several rows of cork tissue, which are exfoliating at the surface. In the mature stem indications of tannin are obtained in abundance in the pith parenchyma, medullary rays, cambium zone, phloem, cortical parenchyma and suberous tissue.

Artificial whalebone is prepared from bones by removing fat, then treating with hydrochloric acid to extract lime; the cartilaginous residue is then steeped in concentrated chrome alum solution until saturated. It is then dried and cut into strips for use.

A CONTRIBUTION TO THE KNOWLEDGE OF SOME NORTH AMERICAN CONIFERÆ.

By Edson S. Bastin and Henry Trimble.

(*Continued from Vol. 68, page 648.*)

TSUGA CANADENSIS.

CHEMICAL COMPOSITION.

Considering the enormous commercial importance of this tree and its products, it has received very little attention by the botanist or chemist. No investigations have been reported recently, except two on the volatile oil, so that the text-books at the present time give the results of observations made from twenty-five to fifty years ago.

The Leaves.—The most important constituent of the leaves is the volatile oil. The preparation of this product was described by Stearns[1] in a report to the American Pharmaceutical Association in 1858. He had, from a practical distiller, the information that in Michigan, at least, the oils of hemlock and spruce (Picea nigra) were one and the same thing, and distilled from the boughs of Tsuga Canadensis, a statement which is probably true to-day.

"The proceeding is as follows: The trees are cut down and the boughs collected only; they are cut up fine and subjected to a distillation with water, in a portable copper still and worm, capable of holding about one hundred gallons, which is so arranged that it can be transported in the woods, and erected quickly upon a temporary arch; two pails full of boughs (about 8 pounds) are calculated to yield 1 ounce of oil. The distilling is done only in winter, when the tree is richest in oil."

Bertram and Walbaum,[2] in 1894, examined oil of spruce, said to have been prepared from Abies Canadensis (Tsuga Canadensis), and found it to consist of laevogyrate pinene, laevogyrate bornyl acetate (36 per cent.) and a sesquiterpene. It had a specific gravity of 0·907 at 15° C. Carl G. Hunkel[3] considered it a question whether this sample was derived from Tsuga Canadensis, or from Picea nigra; he, therefore, collected the leaves and twigs of Tsuga Canadensis himself in the month of September, and submitted them, while fresh, to distillation with water vapor. The yield was small, of a yellowish

[1] Report on the Medical Plants of Michigan, Am. Jour. Pharm. 1859, p. 28.
[2] *Archiv der Pharm.*, 231, 294.
[3] *Pharmaceutical Review*, 14, 34.

color and it possessed the characteristic odor of hemlock. The specific gravity of the dried oil at 20° C. was 0·9288, $[a]_D = -18·399°$ at the same temperature. His conclusion was that this oil of hemlock was very similar in composition to that examined by Bertram and Walbaum, and also to the oil of black spruce, Picea nigra, previously examined by himself.

Our own experiments on the leaves have been limited to an estimation of the tannin, resin and ash. For this work the leaves were collected in November, and, after a short exposure to dry air, were found to still contain 12·80 per cent. of moisture. The ash estimated on absolutely dry substance was found to be 3·78 per cent., and tannin, similarly calculated, amounted to 1·48 per cent. The ash contained calcium and potassium sulphates, phosphates and traces of carbonates and chlorides. The leaves submitted to the action of absolute alcohol yielded 22·97 per cent. of their weight to that solvent. From the residual extract, after recovery of the alcohol, petroleum ether removed 5·83 per cent. of the weight of the leaves, consisting of fat, volatile oil, wax, chlorophyll and resin. Water then removed from the residual alcohol extract 14·70 per cent. of the weight of the leaves, which consisted of tannin, sugar and extractive, leaving 2·44 per cent. of resinous matter and chlorophyll.

The Root Bark.—This portion of the hemlock was collected for examination on the first day of August, and yielded the following results:

	Per Cent.
Moisture	11·83
Ash in dry bark	3·96
Tannin in dry bark	24·46

This large amount of tannin was equivalent to 21·57 per cent. in the air-dry sample.

The Trunk.—The wood portion of the hemlock tree supplies the chief amount of the resin, which is found in commerce under the name of Canadian pitch.

Probably the first pharmaceutical literature concerning this resin was by Charles Ellis,[1] in 1830, and the full title of the paper, as

[1] "Pinus Canadensis, Willd.; Abies Canadensis, Mich. Sylv. A large tree belonging to the natural order Coniferæ, Monœcia, Monodelphia of Linnaeus. Officinal Resin Pini Canadensis. Hemlock Resin. By Charles Ellis." *Journal of the Philadelphia College of Pharmacy*, Vol. 2, p. 18.

given in the foot-note, indicates that the tree and its products were not well known at that time. The paper opens by stating this tree is "known only in the United States by the name of hemlock spruce, and in Canada by the French is called pèrusse." That the resin had not been an article of commerce very long is indicated by the following: "The resin which exudes from it was first introduced into this City (Philadelphia) about twelve years since, and was obtained in this State (Pennsylvania) near Silver Lake, Susquehanna County. But its history even here has been but little known, and still less elsewhere." That the wood of the hemlock was not much esteemed is evidenced by the statement that "of all the great resinous trees of America, its wood is of least value." The process of collecting the resin at that time was different from that given by more recent writers. Then it was prepared by boiling the bark with water and skimming off the melted resin as it rose to the surface. The quantity yielded by a single tree with this process was said to be from 4 to 6 pounds. The product was more or less contaminated with pieces of bark and was submitted to a process of purification by melting and straining.

A more recent report, by Stearns, in 1858, already referred to, gives the process of preparation as wholly from the wood, two methods for this purpose being employed, one by making cup-like incisions in the body of the living tree and allowing the resin to flow out, after the manner of collecting turpentine; the other, by chopping out the knots in the wood, which are rich in resin, and boiling them with water. The latter method is not considered as good as the former, as the boiling with water deprives the resin of most of its volatile oil, which is present in the resin obtained by exudation.

Canada pitch is considered to be equal, if not superior, to Burgundy pitch in the manufacture of plasters; but both have given way, in the modern methods, to caoutchouc and asphalt, chiefly the latter.

Very little is known of the chemistry of Canada pitch; the volatile oil contained in it is probably similar to that obtained from the leaves, and just described; but the resin or resins, which constitute a large proportion of it, have not been studied.

The bark of the trunk is, from both chemical and industrial standpoints, of great importance; nevertheless, there does not ap-

pear to have been published anything concerning its composition. It is evident that it contains resin, volatile oil and tannin, and a closer examination will show the presence of a considerable amount of red coloring, as has already been shown in the description of microscopical structure.

The following results were obtained by us on a sample of bark collected in June, 1896, in eastern Tennessee. The sample was taken from the trunk of a large tree, near the ground, and represents an average sample of the hemlock bark used in that district by tanners. The whole bark was taken; that is, it had not been "rossed." After having been finely powdered, 50 grammes were submitted successively to the following solvents, moisture and ash being added in the proportions they were found to exist in the air-dry drug:

	Per Cent.
Petroleum ether dissolved	0·70
Ether "	3·50
Absolute alcohol "	15·74
Water "	3·92
Alkaline water "	7·51
Acid " "	0·81
Boiling " "	1·47
Ash in air-dry bark	1·42
Moisture in air-dry bark	6·73
Residue and undetermined	58·20
	100·00

The petroleum ether extract consisted of 0·036 per cent. volatile oil, 0·564 per cent. of fat melting at 50°, and 0·10 per cent. of wax melting at 65°.

The ethereal extract consisted chiefly of resin and red coloring matter, with a small amount of tannin.

The alcohol extract contained 7·90 per cent. of resin and decomposed tannin, known as hemlock red, the balance being pure tannin, soluble in water.

The water extract contained neither mucilage, sugar nor tannin, and only a small amount of coloring matter; its composition was not further studied.

The alkali extract contained 2·29 per cent. of albuminoids, and the hot water extract consisted almost entirely of starch.

The ash was found to be composed of magnesium in greatest abundance, aluminum, calcium, manganese, potassium and traces of phosphoric, hydrochloric and sulphuric acids.

It will be seen from this analysis of the bark that the important constituents are tannin, resin and hemlock red; all of these constituents vary with the season of the year. Hemlock red may be an intermediate product between the resins and the tannin; its proportion in the bark is very variable.

HEMLOCK TANNIN.

The tannin of hemlock bark has received so little attention at the hands of investigators, and is of so much importance industrially, that it is considered worthy of especial notice here.

Occurrence.—The few results that have been published concerning the amount of tannin in hemlock bark are widely at variance with one another. Procter[1] says it contains nearly 14 per cent.; he probably quoted Mulligan and Dowling,[2] who, in 1859, found 13·9 per cent. Mafat,[3] 1892, gives 8 to 10 per cent. as the average amount. The following results will show that there may be a great variation in the proportion present, according to the season of the year and other circumstances:

PERCENTAGES OF MOISTURE, ASH AND TANNIN IN THE BARK OF TSUGA CANADENSIS.

Date of Collection.	Moisture.	Ash in Absolutely Dry Bark.	Tannin in Absolutely Dry Bark.	Remarks.
May 12, 1895 . . .	20·06	1·46	8·22	Small tree. Near Philadelphia.
June 30, 1895 . . .	15·54	3·03	9·82	Taken from a branch. " "
August 1, 1895[1] . .	10·00	2·51	14·77	Small tree. Bark from trunk. " "
October 27, 1895 .	11·90	1·21	15·12	" " " " " " "
November 28, 1895	14·01	1·43	15·45	Medium " " " " " "
January 17, 1897 .	13·45	1·58	13·05	" " " " " " "
May, 1896	10·73	1·56	10·60	Large " " " " Tennessee.
June, 1896	10·43	1·40	14·96	" " " " " "
July, 1896	10·98	1·29	11·34	" " " " " "

[1] This sample was taken from the same tree that yielded the root bark, the composition of which has been given on a previous page of this article.

Hemlock bark is usually collected during the months of May, June and July, and the three samples in the foregoing table which

[1] *Text-Book of Tanning*, p. 31.

[2] *Chemical Gazette*, 17, 430.

[3] *Bulletin de la Société industrielle de Mulhouse*, 62, 130. AM. JOUR. PHARM., 64, 531.

were collected in 1896 were taken from similar trees for the especial purpose of determining their relative tannin value.

Preparation.—For the purpose of investigating its composition and properties, a considerable quantity of the tannin was prepared by extracting hemlock bark with acetone. The solvent was recovered by distillation and the syrupy residue was poured into several times its bulk of water; the insoluble resin and anhydrides were separated by agitation with paper pulp and filtration. The clear aqueous liquid was saturated with sodium chloride and shaken with acetic ether, which removed the tannin,[1] the solvent in this case being removed by distillation under reduced pressure. The residue was redissolved in water, salt added and the tannin again removed by acetic ether, and the operation repeated until a tannin resulted which formed a clear solution with water. It was then treated with absolute ether, in which it was insoluble, and, after removal of the ether, dried.

Properties and Composition.—The product was a reddish porous powder, completely and readily soluble in water and in alcohol. A 1 per cent. solution gave the following reactions:

Reagent.	Hemlock Tannin.	Chestnut Oak Tannin.	Gallotannic Acid.
Ferric chloride and Ammonium hydrate.	Brownish-green color and ppt. Purple color and ppt.	Green color and ppt. Purple ppt.	Blue color and ppt. Purple ppt.
Ammonio-ferric sulphate.	Brownish-green color and ppt.	Green color and ppt.	Blue color and ppt.
Calcium hydrate.	Pinkish ppt., turning red.	Precipitate turning pink.	Precipitate turning blue.
Bromine water.	Yellow ppt.	Yellow ppt.	No ppt.

A study of the decomposition products of hemlock tannin was made in the usual way. The product resulting from the action of heat on a solution of the tannin in glycerin was identified as

[1] It has since been found that methyl acetate with salt answers the purpose of an immiscible solvent, for the removal of tannin, equally as well as ethyl acetate, and is much cheaper.

catechol. Boiling hydrochloric acid containing 2 per cent. of HCl gas, resolved the tannin into an amorphous, reddish-brown, insoluble phlobaphene and soluble protocatechuic acid. The phlobaphene was of the same character as that obtained from the tannins of several oak barks. When heated with fused potassium hydrate the tannin yielded protocatechuic acid. Although the above reactions and decomposition products indicated a great similarity between the tannins of the barks of the hemlock and oaks, an ultimate analysis was made in order to further establish their relationship. The results which were obtained show that the tannins from these two sources are very closely related, if, indeed, not identical. For comparison, the figures which represent the composition of chestnut oak bark tannin, gallotannic acid and the average composition of the tannins from nine species of oak bark are given:

	Hemlock Tannin.	Chestnut Oak Tannin.	Average on Tannins from Nine Species of Oaks.	Gallotannic Acid.
Carbon	60·09	59·69	59·79	52·17
Hydrogen	5·18	5·06	5·08	3·10
Oxygen	34·73	35·25	35·13	44·73
	100·00	100·00	100·00	100·00

The several tannins used in the combustions were dried at 120° C.

The conclusion from this study of the properties and composition of hemlock tannin is that it is identical with the other tannins of this natural order, which have thus far been studied by us, as well as with the tannin of oak bark, and a number of others from a variety of sources.

The only other investigation of hemlock tannin on record was made by Boettinger[1], in 1884, who, by precipitating a commercial extract of hemlock bark with bromine, and estimating the halogen in the product, deduced the formula $C_{20}H_{14}Br_4O_{10}$ from which he concluded that the tannin had a composition expressed by the formula $C_{20}H_{18}O_{10}$. Such a formula would require the following percentage composition:

C	57·41
H	4·31
O	38·28
	100·00

[1] *Berichte der deut. chem. Gesell.*, 17, 1041 and 1123.

This is a considerable variation from our figures given for hemlock tannin and, in fact, from those of a larger number of other tannins, and it appears reasonable to attribute this difference to the fact that Boettinger operated on a commercial extract of hemlock. To those familiar with the manufacture of tanning extracts this would be a sufficient reason for allowing his results to await further research on the bark. Much assistance on the chemical investigation of this tannin was given by J. C. Peacock and W. E. Ridenour, who also aided in the collection of the various samples used in the estimations.

ECONOMICS.

When Ellis wrote concerning this tree in 1830, the wood was considered of very little value, but the steady diminution of our forests has brought this wood to the front, and it is now one of the most important lumber trees in northeastern United States. The hemlock trunks also found use before iron became so cheap, in conveying water. A case was reported in 1862[1], where pipes of this wood had been in service thirty-two years, and where the earth was moist they had not decayed. The resin has had extensive use in the manufacture of plasters, and is still employed for that purpose. The volatile oil from the branches is used as a flavoring and for disinfecting purposes. The bark is used to an enormous extent in the manufacture of heavy leather. In recent years, many tanneries have been built in the hemlock districts, so as to be near the supply of bark. For the finer grades of leather the hemlock bark is mixed with that of the oak, in order to avoid the reddish color produced by the former.

An extract of the bark is employed by tanners in place of the bark, or to strengthen their bark liquors, and in a variety of other ways, notably by dyers, in conjunction with logwood coloring, to modify the shades of the latter, especially when copper sulphate is used as the mordant. Large quantities of hemlock extract go to the European markets, where it finds ready sale. All parts of the tree are used except the root, and from what we have seen of its contents of tannin we may look forward to the day when it, too, will not be allowed to go to waste.

(*To be continued.*)

[1] AM. JOUR. PHARM., 34, 377.

CORRESPONDENCE ON THE MANUFACTURE OF SOME GALENICALS FROM FLUID EXTRACTS.

By Edward R. Squibb, Charles Rice and John Uri Lloyd.

Brooklyn, N. Y., January 8, 1897.

Mr. L. F. Kebler, Philadelphia.

Dear Sir:—Your favor of yesterday is received. I am not in a condition to enter upon this discussion, but must confine myself to my chief argument against the general practice of making tinctures from fluid extracts; and this single argument has been sufficient to control my practice ever since fluid extracts were introduced.

The objection to the practice is that it is not authorized by the U.S.P., and that, therefore, such tinctures are not officinal, but are substituted for the officinal tinctures.

To make them so is to break through our own authority, or law, as to how they should be made, and to substitute them for the U.S.P. tinctures is an immoral act of dangerous influence and example.

The convenience of such a practice has been known to the successive Committees of Revision ever since fluid extracts were admitted to the U.S.P., since the practice antedated the admission, and in some of the committees, at least, it was fully discussed and rejected by majority vote. A prominent reason for rejecting the practice was that it doubled the risks of quality in the tinctures so made, and pushed the responsibility for quality back from the dispenser to some one behind. If a dispenser makes a tincture from a drug, he is bound to know, and does know, whether it be the officinal drug or not, and responsibility for the quality of the tincture is direct and, therefore, right and proper. If he makes his tincture from a fluid extract, according to the formula of the fluid-extract maker, he goes entirely behind his only legitimate authority, the U.S.P., both for material and process, and supposes he avoids the responsibility for quality. If he says: "I buy standardized fluid extracts because they are better than unassayed drugs," he brings the practice to depend on the standardization, which is still further back from the legitimate responsibility, for then, who standardizes the standardizer, and who authorizes his assay process?

When the Pharmacopœia finds a set of assay processes simple

enough to be trusted for general use, it will probably direct some such practice. It has not done so yet, and until it does it is but right, and it is the part of wisdom and safety, to conform to its authority and obey its commands. Why sacrifice the advantages of having an excellent Pharmacopœia by trying to set up individual or popular authority against it. Change the law, if you will—but don't change the practice against the law.

I have no objection whatever to your using what I have said in your approaching discussion of the subject on the 20th. Indeed, I would very much like to have this letter read in the discussion at the Pharmaceutical Meeting on January 20th, and published in the Minutes of the College Meeting. Very truly yours,

E. R. SQUIBB.

NEW YORK, January 9, 1897.

Lyman F. Kebler, Esq.

MY DEAR SIR:—You ask me what my opinion is regarding the propriety of making tinctures and other liquid preparations from the corresponding fluid extracts, citing as an example the case of nux vomica, where the U.S.P. directs the tincture to be made from the assayed extract, and then raising the question why a tincture of aconite (35 per cent.) prepared from an assayed fluid extract should be less reliable than one made direct from the drug of unknown strength.

In compliance with your request, I submit the following, which you are at liberty to use, as coming from me, in any way agreeable to you:

When fluid extracts were first suggested and introduced, the principal claim made for them was that they represented the corresponding tinctures, wines, etc., in a more concentrated form and in a smaller bulk. No one claimed for them a different therapeutic action, except, of course, that a proportionately smaller quantity of them was required to produce the same effect as a corresponding dose of the respective tinctures. No authority in therapeutics to this day has maintained that tinctures and fluid extracts prepared from the same drug differed by more than the degree of effect, except, perhaps, in a few cases, and then for reasons well understood.

Now, if a tincture or a fluid extract is properly made from the same, uniformly mixed and comminuted lot of a drug, either of them

should and will contain all the desired active principles of the drug. If this is true, it follows logically and necessarily that if such a fluid extract be diluted by the proper menstruum to the strength of the corresponding tincture, the resulting dilution will be equal in therapeutic effect to the latter. But one reservation must be made here. The equality will be disturbed, if the liquid added as diluent to the fluid extract causes such a disturbance of the dissolved matters that some of the latter, either at once or gradually, lose their solubility and become precipitated. That there are drugs behaving in such a manner cannot be denied, and it must, at the same time, be stated that, while the matters first thrown out of solution are probably, *in themselves*, always inert, yet they are apt to carry along with them some of the useful, active constituents, thereby causing the tincture made by dilution from the fluid extract to become weaker in therapeutic strength than that made originally as a tincture from the drug direct. Moreover, it is well known that when such precipitation once begins, it is liable to progress for a long time, so that even filtration will not interrupt the process of deterioration. A notable example of this class of drugs is cinchona bark, particularly the red variety.

If the statements thus far made are agreed to, it seems to me that we may formulate a few propositions regarding the subject, which will probably also be accepted, though there is likely to arise a difference of opinion as to whether it is practicable at all, or at least as to how far it is practicable to apply the propositions. It should be understood that in comparing any fluid extract and tincture made from one and the same drug, they are assumed to have been prepared from known quantities of the drug of known strength, and, therefore, to be commensurate. The propositions which I wish to make are as follows:

(1) If a fluid extract differs from a tincture only in the quantity of the solvent or menstruum, and if the dilution of the former to the strength of the tincture by the addition of more of the solvent throws nothing out of solution, the two tinctures must be alike in the quantity of active constituents, and, therefore, be alike in therapeutic effect.

(2) If the dilution of a fluid extract to the strength of the corresponding tincture by the addition of even the most favorable menstruum causes a precipitation, the two tinctures may still be re-

garded as alike in therapeutic effect, if the precipitate contains none of the useful medicinal constituents.

These propositions are almost self-evident, and will probably not be gainsaid. But it is a well-known fact that, in many cases, the dilution of a fluid extract produces, sooner or later, more or less precipitation. And as it is not at all practicable to classify drugs into groups representing such as will or will not yield precipitable fluid extracts, though it is possible to *mention* some from which no precipitate is derived, it seems to me unwise to give a general endorsement to the practice of preparing tinctures from fluid extracts, at least at the present time, and in the present state of our knowledge. If the manufacturing houses could put on the market fluid extracts of full official strength, made with menstrua, the further addition of which would cause no precipitate, or at most only one known or guaranteed to be inert, the practice might be approved. But as this is not the case, nor likely to happen in the near future, no general license to make tinctures from fluid extracts should be given. On the other hand, if a pharmacist has the knowledge and ability to examine and assay his preparations, and is willing to assume full responsibility for the quality of the medicines he dispenses, he should have full liberty as to how he arrives at any preparation, say at a tincture, and it is then immaterial whether he prepares it from the fluid extract or the drug. I would, therefore, offer as a third proposition the following:

(3) The practice of preparing tinctures from fluid extracts, in all cases where dilution causes obvious physical changes (such as precipitation, gelatinization, etc.), is not to be recommended for general use, but may be adopted in cases of necessity or urgency, when a prescription calls for the tincture of a drug of which only the fluid extract is available or obtainable.

Now as to the labels you sent me. To judge from experience, I should say that no trouble will be encountered in preparing a tincture from the fluid extracts of aconite and ipecac. But it is probable that some precipitate will form in the case of belladonna leaves and coca leaves, particularly as different persons are apt to use different menstrua, in spite of your direction. Still, we should not pay any attention to what may happen if your directions are disobeyed. If it can be shown that the precipitate in these cases is free from alkaloids, there can be no objection raised against the method.

I have been more profuse than I intended; but I do not regret it now, since it gave me a chance to discuss a subject which has often been brought to my notice. Very truly yours,

CHARLES RICE.

CINCINNATI, O., January 9, 1897.

MY DEAR MR. KEBLER:—Permit me to strongly urge you *not* to commit yourself without reserve to the tincture-from-fluid-extract method. In my opinion there is more than one side to the subject. In the case of preparations in which the therapeutical constituent or constituents of the drug are firmly established and known, and in which no question exists concerning the exact value of the fluid extract, there seems to me to be no question but that the tincture may be made by diluting the fluid extract; this, of course, being in cases where the menstruum will not be considered at all as a therapeutical part of the product.

In such cases as nux vomica, where the therapeutical constituents are permanent, I will go further, and say that, owing to the difficulty of extraction, in my opinion, unless the tincture is assayed in order to establish its value, the method of preparation from an unexceptional fluid extract (standardized) is to be preferred to blind extractions from a standardized drug.

In some cases, however, as, for example, ipecac, I question if it has been demonstrated that a standardized fluid extract will retain its therapeutical value as fully as will the drug. Indeed, I am of the opinion that the advantage is decidedly with the drug. Hence, in such cases as this, which might be illustrated more markedly, perhaps, with other drugs, the element of time may play an important part in the subject

On the other hand, with drugs that deteriorate more rapidly than a bottled preparation made promptly from the drug when in its best condition, the *preference* must, in my opinion, rest with the fluid extract. Among these may be cited those substances containing volatile bodies that escape by age; as, for example, pennyroyal, peppermint, etc. (of course, the fluid must carry full amount of tannates, etc.), and included in this class must be such substances as disintegrate on exposure in drug form, as exemplified in pulsatilla, arum, etc.

Passing now to the great class of drugs in which nothing has been

recorded as to the therapeutical constituents, and in which the menstruum employed in making the official tincture is different from that used in making the fluid extract, in my opinion the question is open yet, and I hardly venture to express a view for or against. Indeed, I would prefer to place these among EMERGENCY preparations, in which, in cases demanding prompt action, the making of a tincture from the fluid extract is permitted, but in which the general stock should be made, as yet, from the drug.

Among the preparations where tinctures may be made, I would include all these fluid extracts *not official* and of which no standard menstruum exists for making either the tincture or fluid extract. These the pharmacist should be permitted (expected) to mix from the respective fluid extract when he has a call for the tincture.

Finally, in cases where the menstruum directed by the U.S.P. is decidedly different from that used in making the fluid extract, especially in those cases where the tincture is given in large doses and in which the alcoholic strength of the tincture is very much less than that of the fluid extract, the question of therapy extends beyond the drug question. If the fluid extract is mixed with the official menstruum, an unscientific product results; if it be not mixed with the tincture menstruum, the superabundance of alcohol may prove objectionable. In these cases, until the U.S.P. is corrected and identical solvents used in making both tincture and fluid extract (which, in my opinion, should be accomplished, and with few exceptions can easily be done), the making of the tincture from the fluid extract should be avoided, unless an emergency case renders it absolutely necessary, which now and then will be the case.

In my opinion this subject is one worthy of some study and consideration. I see no reason why manufacturers of fluid extracts should not give directions for making tinctures from fluid extracts; but, in my opinion, although such information is useful in emergency cases, and in certain cases to be *preferred*, I would not advocate the substitution of a line of tinctures made in this way without Pharmacopœial authority. I feel that the skill required in making these simplest of pharmaceutical preparations is not such as to prevent their preparation from the drugs, and I believe it is the duty of the Pharmacist to make them according to the Pharmacopœia, until the Pharmacopœia gives him the privilege of selecting either method. This, I believe, in face of the fact that in my opinion cer-

tain tinctures can in a general way be made as reasonably (or even cheaper) from the fluid extract, and with greater uniformity than from the drug. Of course, you are at liberty to use this letter in your society if my personal opinion will be of service. Bear in mind that the subject is considered in a rambling way and superficially, but still it voices opinions gained by more than a little thought in this direction. Very sincerely yours,

JOHN URI LLOYD.

PURE SPERMACETI.

BY LYMAN F. KEBLER.

About a year ago, the writer presented[1] some data on the question of spermaceti. The conclusions arrived at then raised a question concerning the absolute purity of the material operated on. While it was impossible to state that the spermaceti was absolutely pure, yet there was every reason to think that such was the case. In order to settle the question as completely as possible, specimens of spermaceti were secured as close to the natural source as the nature of the case permitted. To bring this about most effectually, every person who was likely to be in a position to secure a sample of pure material was interviewed, either personally or through correspondence. The original producers were also requested to furnish samples that they were willing to guarantee absolutely pure. This they cheerfully did.

By the above procedure, three specimens were received from the Pacific Coast, through the kindness of Prof. W. R. Searby, of San Francisco, Cal. Prof. E. L. Patch, kindly secured a sample himself at New Bedford, Mass. Profs. J. P. Remington and W. R. Scoville each obtained a sample from the same source, through friends closely connected with the spermaceti trade there. The writer himself secured five samples from the original producers, with guarantees of absolute purity. Dr. Chas. Rice also assisted in the way of suggestions. No. 12 was a specimen obtained by melting together several samples taken from a purchase of 2,000 pounds. These specimens, coming directly from the centres of supply of the United States, can reasonably be expected to be pure, at least purer material cannot be secured in this country.

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[1] 1896, AM. JOUR. PHARM., 68, 7.

Having accumulated the samples, they were carefully examined. Physically, they resembled one another very closely, and did not differ in any respect from the commercial material examined during the past three years. They were all tested in the same manner that those reported on last year were; in addition, however, the specific gravity was taken in a liquid lighter than the spermaceti, by means of the sinker attached, and at the boiling point of water in a pycnometer. Two methods for attaching the sinker were employed. In the first case, the sinker was simply tied to the spermaceti; in the second case, the sinker covered the spermaceti so that only one surface was exposed to the liquid, thus reducing the question of attached air-bubbles to a minimum. This was done in the following manner: Porcelain crucible covers were carefully cleansed, dried and their weight taken. The melted spermaceti was poured into these covers, allowed to cool at the temperature of the working-room and the specific gravity taken at the end of two days with the spermaceti *in situ*. The congealing points were also observed. The results are as follows:

Persons Secured Samples.	Melting Point, C.	Congealing Point, C.	Acid Number.	Ether Number.	Specific Gravity at 98°–99° C. Water at 98°–99° C.	Specific Gravity at 98°–99° C. Water at 15° C.	Specific Gravity at 15° C., in Alcohol.	Specific Gravity at 15° C., Sinker Attached.	Specific Gravity at 15° C., Spermaceti in Sinker.	Specific Gravity at 15° C. by Suspensory Method.
Remington . .	43·5°	42°	0·47	129 62	0 8406	0·8083	0·8981	0·8979	0·8902	0·9381
Scoville . . .	44·5°	43°	0·10	125·	0·8405	0·8083	0·8989	0·8992	0·8987	0·9385
Patch	45°	43°	0·25	124·8	0·8404	0·8082	0·9042	0·9009	0·9036	0·9401
Searby	44°	42·5°	0·21	131·06	0·8458	0·8124	0·9066	0·9007	0·8954	0·9510
Searby	43°	42°	0·16	136·31	0·8432	0 8109	0·8960	0·9099	0·8118	0·9413
Searby	43·5°	42°	0·43	129·91	0·8432	0·8160	0·8969	0·9000	0·9009	0·9420
Kebler	44°	43°	0·30	130·30	0·8412	0·8089	0·8960	0·8972	0·8993	0·9394
Kebler	43°	42°	0·35	130·20	0·8412	0·8089	0·8899	0·8974	0·8937	0·9400
Kebler	44°	43°	0·23	125·81	0·8410	0.8087	0·8982	0·8983	0·8982	0·9421
Kebler	46°	44·5°	0·19	129·02	0·8412	0·8089	0·9079	0·9079	0·9013	0·9410
Kebler	44·5°	43°	0·29	128·13	0·8419	0·8097	0·9103	0·9018	0·8992	0·9500
Commercial .	44°	43°	0·09	125·1	0·8409	0·8093	0·8991	0·8993	0·9010	0·9400

The melting-points, acid numbers and ether numbers correspond very closely with those reported last year. The anomalous specific gravities are unique and require an explanation. The highest specific gravities were obtained by the same method that was used to ascertain the specific gravities reported on in a previous paper, viz.: alcohol diluted to such an extent that the small pellets floated indifferently. This method, for convenience, will be called the *suspensory method.*

In making the pellets for the suspensory method, the melted (on a water-bath) spermaceti was dropped on a moistened plate having a temperature of about 20° C. This was cool enough to chill the melted spermaceti quickly, so that the molecules were not given time to assume a crystalline form; at least, the pellets were very slightly crystalline, if at all.

For the other methods in which the solid material was employed, the melted spermaceti was poured into porcelain crucible covers and allowed to cool in a room at about 22° C. After cooling, the spermaceti was removed from the covers. All material worked on was given at least two days' time to assume a normal state before the specific gravity was taken. These prepared forms were 30 mm. in diameter and about 6 mm. thick; thicker in the centre, tapering towards the circumference. The manner of congealing allowed ample time for the spermaceti to assume crystalline forms.

Normally, spermaceti is crystalline. From the fact that the pellets prepared for the suspensory method were non-crystalline, and of a higher specific gravity than the crystallized material, the writer is led to think that the specific gravity for normal spermaceti is not much above 0·9000 and not much below 0·8900 at 15° C. The specific gravity obtained by the suspensory method is probably abnormal, due to the non-crystalline character of the pellets.

The writer, on referring to his memorandum, finds that the low specific gravities obtained by the suspensory method, reported in a former contribution (0·905, 0·915, 0·920, etc.), were taken during the months of August and early September; while the higher specific gravities (0·935, 0·939, etc.) were taken in November and December.

In the former case the elevated temperature was conducive to the formation of more highly crystalline pellets than in the latter case, when the temperature was considerably lower. The specific

gravities embodied in the present paper were all taken during the cold weather of December, 1896.

To throw further light on this point, further observations were made. The writer has in his possession a sample of crude sperm oil; on cooling, spermaceti crystallizes out and floats indifferently on the liquid at about 22° C.; the specific gravity of this mixture at 22° C. is 0·8846, which would approximate 0·8900 very closely at 15° C. Next, a sample of spermaceti, having a specific gravity of 0·9385 at 15° C. by the suspensory method, was dissolved with 20 per cent. of paraffin, having a specific gravity of 0·9132 at 15° C. by the same method. This mixture possessed a specific gravity of 0·945 by the same method. The same spermaceti, with an admixture of 33 per cent. of paraffin, had a specific gravity of 0·946 at 15° C. by the suspensory method. The experiments again indicate that the conclusion arrived at above is correct.

In view of the possibility of obtaining such variable results for the specific gravity of solid spermaceti it is necessary to detail exactly the conditions under which the observations are made, or the results are worthless.

The writer recommends that the specific gravity of this substance be taken at the boiling point of water. The results by this process are uniform and concordant. This is done as follows: Pour the melted spermaceti into the warmed pycnometer, insert the stopple and plunge the bottle immediately into boiling water, to such a depth that the neck of the bottle only projects. Keep the water boiling for one hour, remove the bottle, wipe well, cool and weigh.

This gives the weight of a given volume of spermaceti at the temperature of boiling water.

The conclusions arrived at in the previous article are fully supported by the observations made in this communication, except the specific gravity of the solid material. To this constant a greater degree of variableness must be ascribed, depending entirely on the crystalline or non-crystalline condition of the spermaceti operated on.

Before closing the writer desires to kindly thank all who assisted him with this work.

305 Cherry Street, Philadelphia, Pa.

SOLNINE NOTE.

By John Uri Lloyd.

The *American Journal of Pharmacy*, April, 1894, contained a paper from my pen concerning the alkaloid of *Solanum Carolinense*. To this alkaloid I ventured to affix the name *Solnine*, "in order to give it an existence in literature." I also stated that "having never made a study of *Solanine*, I am not prepared to decide concerning the identity of *Solnine* and that substance. If Wittstein's description of *Solanine* is correct, they are different." Afterward (September, 1895) a determination was accurately made of the melting point of crystallized solnine. This, together with the characteristics noted in the paper of April, 1895, may be said to fairly establish that Solnine is not the same as Solanine.

Melting point of Solnine . . . . . 127·2° C.
Melting point of Solanine (as per current literature) . . . . 235·0° C.

A fresh supply of Solnine is now in process, and then I hope to supply combustion figures.

PILOCARPINE HYDROCHLORIDE.[1]

By Dr. B. H. Paul and A. J. Cownley.

In the last issue of the Pharmacopœia of the United States of America an addition was made to the characters of this salt by giving the melting point as 197° C., and an American journal has recently expressed the opinion that an observation of the melting point is the best means of ascertaining the purity of the salt met with in commerce. It might therefore be inferred that the hydrochloride has in that respect an advantage over the nitrate, some samples of which we have shown differ considerably in the melting point. The question, however, is not so much as to the purity of any particular salt, but whether the alkaloid obtained from jaborandi consists of more than one chemical individual. The results already described by us[2] point to the probability that the salts met with in commerce under the name of pilocarpine nitrate do contain more than one base, and there is consequently some uncertainty as to which of those bases has the medicinal action peculiar to jaborandi.

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[1] *Pharmaceutical Journal*, November 21, 1896.
[2] *Pharm. Jour.*, 1896, p. 1. Am. Jour. Pharm., 1896, p. 445.

A similar want of homogeneity might be expected to obtain with the hydrochloride and other pilocarpine salts.

In examining some samples of pilocarpine hydrochloride as to the melting point, we have found that this salt gives indications of being a mixture of more than one chemical compound. Taking the melting point in a Roth apparatus, we found that two different temperatures might be read as the melting point, one at which the substance in the capillary tube showed signs of partial liquefaction, and a higher point, at which the contents of the tube became entirely liquid. The results obtained with two samples of pilocarpine hydrochloride are given in the following table:

Sample.	Began to Run.	Clear Liquid.
A	192·7°	196·7°
B	192·2°	196·7°

This behavior appears to point to the probable presence of two substances in both of the samples, judging from the partial melting at the lower temperature, and the way the salt becomes a clear liquid at a point about 4° higher.

For one of these samples of pilocarpine hydrochloride we are indebted to Messrs. Domeier, who were good enough to procure it specially from the makers, Messrs. C. F. Boehringer & Sons. At the same time they sent an account of the result of some pharmacological examinations they have had made in consequence of the statement as to abnormal action of pilocarpine salts.[1] They have found that a salt of high melting does not differ in its action from the one of low melting point which can be separated by purification—presumably fractional recrystallization. In regard to the medicinal use of pilocarpine salts, this result would appear to show that the possible presence of two substances is, from that point of view, a matter of no account; but, at the same time, it would do away with the value of the melting-point test as a criterion of the qualities of pilocarpine salts.

In reference to the abnormal action of pilocarpine salts analogous to that of atropine, Messrs. Boehringer suggest that it may probably be due to the presence of jaborine; but as the existence of that base is somewhat questionable, such a mode of explanation would require to be supported by more definite proof than is at present available.

[1] *Ibid.*, p. 2.

RECENT LITERATURE RELATING TO PHARMACY.

NOTES ON THE TREES YIELDING MYRRH.

E. M. Holmes read an interesting paper on this subject at an evening meeting of the Pharmaceutical Society, of Great Britain (*Pharmaceutical Journal*, December 12, 1896), in which he detailed his own investigations and at the same time incorporated some literature on this subject, which appeared in the *Kew Bulletin* for March and April, 1896.

Myrrh is imported into England chiefly from Aden, to which port it is sent from Arabia and Abyssinia. Some comes from Bombay, and is known in the London market as "red Zanzibar" myrrh. Writers on materia medica distinguish four varieties: Somali myrrh; Arabian myrrh, of Hanbury; Arabian myrrh, of Dymock, or Meetiya, and Yemen myrrh. There are also three others mentioned in *Pharmacographia Indica*, I, p. 307, as occurring in the Bombay market: Persian myrrh, sent principally from Mekran, Chinese myrrh and Siam myrrh or Meetiya; the same authority states that myrrh appears to have been shipped from China as early as A. D. 1340.

Judging from the taste and odor of the four principal varieties of myrrh mentioned above, it might reasonably be supposed that they are the product of one species of Commiphora, or of varieties of the same species modified by conditions of soil, elevation and climate.

Concerning the plant which yields Somali myrrh, we have no exact information, for there exists very little evidence connecting the gum resin with the trees supposed to yield, owing partly to the fact that collectors of plants are not usually well acquainted with the drugs of commerce.

With respect to Arabian myrrh the case is different. About the year 1820, Ehrenberg collected specimens of a myrrh tree at Gezan, in South Arabia. These were referred to Balsamodendron myrrha, Nees. Subsequently, however, Berg showed that two species were mixed under this name, and he separated the second, which has obcordate leaflets, under the name of B. Ehrenbergiana, Berg. The first of these, Balsamodendron, or, as it is now called, Commiphora myrrha, has recently been stated by Schweinfurth to yield no resin at all, and the second has been identified as a variety of the Balm of

Gilead tree, C. opobalsamum. Professor Schweinfurth has recently stated that Arabian myrrh is the product of Commiphora Abyssinica, Engl., and of C. schimperi (*Berichte der Pharm. Gesellschaft*, 1893, pp. 218 and 237), but the Director of Kew Gardens, in a lengthy paper on the subject in the *Kew Bulletin*, 1896, p. 91, in which he differs somewhat from the views of Professor Schweinfurth, expresses the opinion that Commiphora simplicifolia may be accepted as the source of Yemen myrrh, and that Fadhli myrrh be yielded by both C. myrrha and C. simplicifolia.

Professor Schweinfurth supplied the herbarium of the Pharmaceutical Society with specimens of C. Abyssinica, C. schimperi, C. simplicifolia, C. Africana and C. opobalsamum, and it occurred to Mr. Holmes that some light might be thrown on this difficult question by tasting the bark and fruits of these specimens, especially as true myrrh has a very bitter taste, and a peculiar aroma, hardly likely to be entirely absent in the plant itself. In none of these did Mr. Holmes detect the odor and taste of myrrh, and he says we are driven to the conclusion that Arabian myrrh is the produce of the plant named Balsamodendron myrrha, by Nees, and not of C. Abyssinica, nor of C. simplicifolia, nor of C. schimperi. There are several acrid gum resins that occur mixed with myrrh as imported. The most abundant of these is opaque bdellium, which, as pointed out by R. H. Parker (*Pharm. Jour.* [3], **11**, p. 41), differs from hotai in its greater toughness, and in giving an intense greenish-black color with ferric chloride. These are, doubtless, yielded by other species of Commiphora. Thirty-five species of Commiphora are described in A. DeCandolle's *Monographiæ Phanerogamarum Prodromi*, Vol. 4, pp. 9–29.

RELATION OF THE GROWTH OF FOLIAGE LEAVES AND THE CHLOROPHYLL FUNCTION.

The following conclusions have been reached by D. T. MacDougal (*The Journal of the Linnean Society*, **31**, 526), after a practical study of a number of plants:

(1) Material constructed in active chlorophyll areas and stored in special organs may be transported to inactive chlorophyll-bearing organs in some plants in light and in darkness, and be used in such manner as to allow of the perfect development of these organs.

(2) The removal of concurrent members in darkness may have

no effect, may cause an exaggerated development of the petioles, or may result in the perfect development of the entire leaf. The nature of the regulatory mechanism in each instance must be entirely specific.

(3) It is possible for some plants to form perfect leaves in darkness, some when a portion of the stem only is darkened, and others when the entire plant is etiolated. It is thus shown that no invariable connection exists between the phototonic condition and leaf-development.

(4) The conclusion of Jost, that pathological conditions ensue more quickly in inactive leaves in light than in darkness, is not capable of general application. The deterioration in certain plants appears as quickly in darkness as in others in light.

(5) Placing a leaf under such conditions that it cannot construct food material, sets in motion the specific regulatory mechanism of the organism in such manner that the plastic material may be withdrawn and the organ cast off. An exaggerated development of the petioles may be induced in darkness by this mechanism.

(6) It is to be noted that plants may not be entirely ? as to their reaction to an atmosphere devoid of CO_2 upon the basis of species, since a given plant may be capable of developing inactive leaves at one stage of its development, and not at another. This is evident upon consideration of the fact that such capacity is entirely dependent upon the availability of the reserve food for this purpose.

In addition to this summary, the article contains an interesting historical introduction and a short bibliography of the subject.

ORANGE GROVES OF NAPLES.

The Orange Groves of Naples are planted with wild trees, which are grafted in the usual way, and grow with bare trunks to 4 or 5 feet from the ground. The branches then run out and form the fruit-bearing portion of the tree. An ingenious and beautiful innovation has been introduced into one grove, and is described by Consul Neville-Rolfe in his latest report. Lemons are grafted upon the bare and non-productive stems of the oranges, about 2 feet from the ground, and trained in garlands from tree to tree, thus not only increasing the productiveness of the grove very materially, but adding greatly to the picturesqueness of its appearance. Orange trees being usually planted in rows at a measured distance apart, a

grove has usually a geometrical appearance which is unsatisfactory, but this appearance is very much modified by the lemons, which break the lines in all directions. There is a legend which most people firmly believe, that the grafting of a second fruit on the parent stem materially alters the type and quality, not only of the original fruit, but also of the graft, and it is sometimes gravely asserted that "blood oranges" are obtained by grafting the pomegranate on to the orange. This, says the Consul, is a complete fallacy. Both fruits retain their original quality, and neither borrows anything from the other. There is thus no difference between the lemons grown in the orange grove from those grown in the grove where lemons alone are cultivated.—*Pharmaceutical Journal, October 17, 1896.*

DETERMINATION OF THEOBROMINE IN CACAO. (Eminger, in *Forschungsberichte*, 1896, 275.)

The author first extracts vegetable fat by digesting 10 grammes of the finely powdered material with 150 parts of petroleum spirit; the residue is then dried and a weighed portion boiled for about half an hour, or until the formation of cacao-red is completed, with 100 cubic centimetres of dilute sulphuric acid (3–4 per cent.) in a flask fitted with a reflux condenser. The contents of the flask are then turned into a beaker and, whilst hot, exactly neutralized with the calculated quantity of baryta; the whole is evaporated to dryness with some sand, and the residue extracted in a Soxhlet apparatus with 150 parts of chloroform for five hours; the chloroform is then distilled off and the residue dried at 100° C. This residue is then washed with not more than 100 cubic centimetres of carbon tetrachloride, which dissolves the fat and caffeine; the theobromine, being quite insoluble in carbon tetrachloride at 18° C., is collected on a filter, dissolved in boiling water, the solution filtered and evaporated and the residue weighed. By this method the theobromine in different kinds of cacao was found to vary from 1·05 to 2·34 per cent., and the caffeine, from 0·05 to 0·36 per cent. Theobromine is soluble in 736·5 parts of water at 18° C., in 136 parts at 100° C., in 818 parts of boiling absolute alcohol, in 21,000 parts of ether at 17° C., in 2,710 parts of boiling chloroform, and in 5,808 parts at 18° C. "Theobromine begins to sublime at 220° C. without melting, whilst caffeine sublimes at 180° C. and begins to melt at 220° C." Theobromine is more or less decomposed if

warmed for any length of time with alkalies, earthy oxides or hydrated lead oxide.—*The Journal of the Society of Chemical Industry, October 31, 1896.*

ANALYSIS OF CHLOROFORM. (*Gay, in J. Pharm. Chim., 1896, 4, 259.*)

(1) A piece of filter paper saturated with the chloroform should dry completely, and the odor remain pleasant to the end. The contrary indicates the presence of amyl alcohol.

(2) Shake 6 c.c. with 3 c.c. of water and test with litmus paper; this should not be reddened.

(3) Shake with an equal volume of 10 per cent. silver nitrate; a white precipitate on standing indicates the presence of hydrochloric acid, and a black precipitate on boiling, that of aldehyde or acetone.

(4) To 5 c.c. add 2 c.c. of a solution of 1 part of potassium bichromate in 100 parts of strong sulphuric acid, and warm gently; if alcohol be present a green coloration appears. A quantitative test for alcohol is necessary, since 0·5 per cent. may be added to preserve the chloroform. To 5 c.c. add 1 c.c. of Mohr's solution (1 part of potassium permanganate and 10 parts of alcoholic potash dissolved in 25 parts of water) in such a manner that the liquids do not mix; then shake whilst slowly turning the tube, and observe the time between the mixture and the appearance of a green color.

Time: 5 minutes	. . . . .	Very pure chloroform.
" 2·5 "	. . . . .	0·01 per cent. alcohol.
" 3·5 seconds	. . . . .	0·1 " "
" 5 "	. . . . .	0·5 " "
" Less than 5 seconds	. . more than	0·5 " "
One agitation	. . . . .	1·0 " "

(5) Shake violently 10 c.c. with an equal volume of strong sulphuric acid and let stand. The mixture remains colorless, even for an hour, if the product is pure, but if it becomes brown, the presence of chloro-derivatives of ethyl alcohol or of the higher homologues is indicated.—*The Journal of the Society of Chemical Industry, October 31, 1896.*

The quantity of quicksilver exported by the mines of Auerbach & Co., at Nikotovka, Russia, in the course of last year, amounted to 10,706 bottles, which went to various European countries, China, India and to the Transvaal. For consumption in Russia 1,596 bottles were sold. The output is steadily increasing.—*Chemist and Druggist,* December 5, 1896.

EDITORIAL.

MINERAL STATISTICS FOR 1896.

The *Engineering and Mining Journal*, of New York, in its issue of January 2, 1897, presents the statistics of the mineral and metal production of the United States for the year 1896. These statistics are gathered from official sources, or from reports of producers, and will be found to be very close to those which are made up later in detail. From these statistics we glean some facts of interest to pharmacists.

Non-Metallic Products.	1895.		1896.	
	Metric Tons.	Value.	Metric Tons.	Value.
Alum	68,025	$2,225,000	72,900	$2,275,000
Bromine	179	102,662	249'5	143,074
Borax	6,126	742,850	6,886	759,094
Copperas	12,805	69,846	10.796	53 112
Copper sulphate	20,412	1,350,000	20,412	1,350 000
Gypsum	270,804	974,219	241,900	867,071
Petroleum, crude	6,420,742	42,547,701	5,731,920	42,116,184
Salt, evaporated	1,539,178	5,844.348	1,391,349	5,432,105
Salt, rock	173.662	518,740	146,998	138,840
Soda, natural	1,724	47,500	—	—
Soda, manufactured	167,000	3,841,000	—	3,500,000
Sulphur	1,676	126,950	1,524	100,000
Metals.				
Aluminum	408	495,000	589'3	520,000
Antimony	393	68 847	579	83.440
Copper	175,294	36,944,988	205,853	48,786,080
Gold	70,470 kilos.	46,830,200	85,773 kilos.	57,000,000
Iron, pig	9.597,449	108 632,542	8,909 000	87,688,690
Lead (New York value)	142,298	10,132,768	159,410	10,472,733
Platinum	150 ozs.	2,250	150 ozs.	2,250
Quicksilver	1,179	1,313,589	1,160	1,222,444
Silver (commercial value)	1,441,087 k.	30,254,087	1,414,148	30.461,665
Zinc (spelter)	74 245	5 942,890	74,925	6,074,219

S. P. S.

FIELD BOTANY IN WINTER.

The *Pharmaceutical Journal*, in its issue of January 2, 1897, says the wild flowers most likely to be found in blossom in England during the early part of January are Capsella Bursa-pastoris, Ulex Europæus and Senecio vulgaris. This leads us to speak of the winter-blooming plants in the United States, where in the latitude of Philadelphia one does not need to await the arrival of spring to pursue outdoor botanical studies, since there is probably no month in the year in which plants cannot be found in bloom in this latitude. It is also of peculiar interest to observe the winter habits of a great number of plants, even if they are not in flower.

A walk of four or five miles in the vicinity of Philadelphia, on November 26, 1896, revealed the following eighteen plants in bloom; they were not unusually protected, although many of them were found on banks having a southern exposure: Sisymbrium officinale, Lepidium virginicum, Stellaria media, Cerastium viscosum, Malva rotundifolia, Trifolium pratense, Daucus carota, Solidago serotina, S. nemoralis, S. rugosa, Taraxacum officinale,

Chrysanthemum leucanthemum, Aster ericoides, A. cordifolius, Antennaria plantaginifolia, Gnaphalium polycephalum, Erigeron Canadense and Lobelia inflata. Two other plants, Symplocarpus fœtidus and Claytonia virginica, were found, which showed the floral organs well developed and only awaiting a suitable time in which to bloom.

On December 31, the following were found in blossom: Taraxacum officinale, Stellaria media, Veronica Buxbaumii, Lamium amplexicaule and Symplocarpus fœtidus.

REVIEWS AND BIBLIOGRAPHICAL NOTICES.

EINFÜHRUNG IN DAS STUDIUM DER ALKALOIDE, mit besonderer Berücksichtigung der vegetabilischen Alkaloide und der Ptomaine. Von Dr. Icilio Guareschi, O. Ö. Professor an der königl. Universität Turin, und Director des pharmaceutisch-chemischen und toxicologischen Instituts. Mit Genehmigung des Verfassers in deutscher Bearbeitung herausgegeben von Dr. Hermann Kunz-Krause, dozent für allgemeine und pharmaceutische Chemie an der Universität Lausanne. Erste Hälfte. Berlin, 1896. R. Gaertner's Verlagsbuchhandlung, Hermann Heyfelder.

In publishing a German translation of Guareschi's "Introduzione allo Studio degli Alcaloidi," Dr. Kunz-Krause has made available to a large number of readers what would otherwise be a sealed book. The first half is now obtainable, and the second half will appear during the year 1897. After a brief introduction, the work very properly begins with a historical review, in which the development of the alkaloids is shown to have been the work of chemists of the nineteenth century. Beginning with the discovery of morphine, by Sertürner, in 1805, this historical summary is divided by the author into six periods, as follows:

Period 1.—Discovery of numerous vegetable alkaloids, 1806–1835.

Period 2.—Investigation of the coal-tar bases (aniline), 1834–1848.

Period 3.—Discovery of pyridine and quinoline bases.

Period 4.—Synthesis of the oxy-ethylene bases and of the paraconiines; theory of the constitution of pyridine and quinoline.

Period 5.—Discovery of ptomaine and leucomaine.

Period 6.—Synthesis of a large number of basic pyridine and quinoline derivatives, and the investigation of the constitution of the natural alkaloids.

The history is followed by a brief description of the properties of the various organic bases and a discussion of their structural relations. Several pages are devoted to the alkaloidal reagents, and the behavior of each towards the alkaloids is explained. Following this is a short summary on classification and nomenclature, in which the great body of the book is divided into five sections, as follows: I, Bases of the Open Chain Series; II, Bases of the Closed Chain Series; III, Metal Amines; IV, Alkaloids in the Narrower Sense; V, Ptomaines and Leucomaines. The present volume is largely occupied by the first two sections, and consequently embraces most of the synthetic organic bases, as well as those natural alkaloids whose structure has been established.

The whole book is very systematically arranged, and furnishes abundant material for prolonged study by everyone who is interested in this important

branch of organic chemistry. It is a great credit to both author and translator, and we look forward with interest to the appearance of the second half.

COMMERCIAL ORGANIC ANALYSIS. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicine, etc., with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.I.C., F.C.S. Second Edition. Vol. III, Part III. Philadelphia: P. Blakiston, Son & Co. 1896.

The installment of this work now published is nominally Part III of Volume III, though practically it forms Volume V of the book. One more volume, treating of proteids and albuminoid compounds, will complete the work. The part now issued treats of the less important vegetable alkaloids, left over from Part II; non-basic vegetable bitter principles; animal bases, including ptomaines; animal acids, and cyanogen compounds. Although considered by the author as less important alkaloids, still there are among them those derived from ipecac, colchicum, calabar bean and jaborandi, which makes them of considerable importance.

The same systematic treatment has been accorded these alkaloids that was given to those in Part II, and it serves to make the two volumes the most important works on this subject in the English language. About one hundred pages are devoted to the non-basic vegetable bitter principles. The literature concerning these important compounds is very voluminous, and the author has sifted that so as to make it available to other chemists. Not the least in this class is his condensed statement concerning the constituents of digitalis, about which so much has been written that in many minds the whole subject is decidedly mixed.

Under the animal bases we have the whole subject of estimating urea as well as the latest information concerning creatine and creatinine; these have also been exhaustively treated in the author's *Chemistry of the Urine*, published over a year ago.

The whole book is fully equal in value to its predecessors, and the final volume is looked forward to with interest.

POPULAR GERMAN NAMES OF DOMESTIC DRUGS AND MEDICINES (Volksthümliche deutsche Arzneimittel-Namen). Compiled by Dr. Fr. Hoffmann. Revised and enlarged edition. Pharmaceutical Review Publishing Company, Milwaukee. 1896.

Dr. Hoffmann has performed a real service for the American druggist by compiling this list of popular German names and arranging them so as to be available to every one but the most stupid. In nearly all parts of the United States the pharmacist is confronted in his daily practice with the German names of many of the simpler drugs. The book can be had of the Pharmaceutical Review Publishing Company, at the moderate cost of fifty cents per copy.

LE COMMERCE ACTUEL DE L'HERBORISTERIE DANS UNE RÉGION DU LANGUEDOC. Par le Dr. Louis Planchon.

Reprint from *Journal de Pharmacie et de Chimie*, 1896. An interesting contribution to the local flora of a region very rich in medicinal plants.

LA COMPOSITION DES PEPTONES DE VIANDE. Par A. Denaeyer. A communication to the second International Congress of Applied Chemistry at Paris. 1896. Reprinted from *Annales de Pharmacie.*

PROSPECTUS OF THE TWENTY-FIFTH ANNUAL SESSION OF THE CALIFORNIA COLLEGE OF PHARMACY. Session of 1897.

MINUTES OF THE PHARMACEUTICAL MEETING.

PHILADELPHIA, January 20, 1897.

The regular Pharmaceutical Meeting was held in the Museum of the College. Mr. J. W. England was chairman. The minutes of the previous meeting were allowed to stand as published.

Professor Trimble called attention to a sample of the genuine kino of Eucalyptus rostrata, which had been sent by Mr. J. H. Maiden, of Sydney, New South Wales; also to a sample of Texas rhatany Kramerie secundiflora, which was collected in Mexico and presented by Prof. Alfonso Herrera; and also to some specimens of cultivated canaigre root, which were grown in California and were unusually large.

Mr. Lyman F. Kebler read a paper on the "Volumetric Estimation of Acetone" (see p. 65), which was considered to be particularly opportune, inasmuch as the various applications of acetone as a solvent have only just begun.

The author stated that the methods for estimating the percentage of acetone were not yet perfected, and that only the amount of iodoform producing bodies could be determined in the commercial product.

Mr. Edward T. Hahn read a paper on "Terpin Hydrate" (see p. 73), and said that his experiments had been made with a view of producing the crystals of this substance, rather than studying its therapeutic properties, or of determining its ultimate composition. Samples which had been made with ethyl alcohol and also with methyl alcohol accompanied the paper.

After the reading of the papers, an interesting discussion on the subject of the manufacture of some galenicals from fluid extracts ensued, and was participated in by Mr. Kebler, Mr. England, Professor Remington and others. The question was introduced at the December meeting by Mr. Kebler, but was deferred on account of lack of time, and in the meantime he received letters on the subject from Dr. E. R. Squibb (see p. 98), Dr. Chas. Rice (see p. 99) and Prof. J. U. Lloyd (see p. 102).

Mr. Kebler prefaced his remarks by saying that the commercial aspect of the question could not be taken into consideration; that human life was too valuable for this phase of the subject to merit any attention in this connection.

He said in considering the merits and demerits of the main subject that "when it comes to the question of making infusions from the fluid extracts, it must be admitted, on the one hand, that it is wrong in many cases, in the light of our present knowledge; but, on the other hand, it remains to be demonstrated that an infusion made from a fluid extract is less active, therapeutically, than one from the drug direct. In some cases an aqueous menstuum will educe active constituents that are insoluble in alcoholic solutions and *vice*

versa. But when we enter the field of manufacturing tinctures and some other preparations from the respective fluid extracts, debatable ground is invaded."

Before taking up this question he deemed it necessary to state that if the position were taken that a U.S.P. preparation was U.S.P. only when made strictly according to the directions therein laid down, and could not be made in any other way, there was only a single answer to the question.

Some of the faulty and imperfect tests and methods of the Pharmacopœia were referred to, as well as some of the duplicate processes sanctioned by it, as in the case of the processes for the manufacture of fluid extracts, and thus the Pharmacopœia itself was considered to justify, in a measure, the application of processes which seemed best adapted to the needs of the case.

Standardized preparations and the manufacture of other preparations from them then claimed the speaker's attention. He said that the 1890 Pharmacopœia had incorporated methods for assaying the crude drugs cinchona, nux vomica and opium, as well as some of their preparations; and that the next revision would, undoubtedly, be enriched by methods for assaying a number of other drugs and their preparations. The assay processes already authorized had been introduced on account of the great variability of the drugs to which they were applied. Then referring to his analytical records the speaker said that these showed that there were other drugs equally variable in character; for instance, one bale of aconite root assayed 0·4 per cent. total alkaloids, and another 1·14 per cent., or one root was nearly three times as potent as the other. It was evident that tinctures and fluid extracts, made according to the Pharmacopœia from these roots, would vary accordingly. In other words, the tincture made from the root containing the high percentage of alkaloids would be as powerful as the fluid extract made from the lower assaying root. This was not an isolated case, but similar data could be furnished for other drugs.

The problem of extracting the active principles from the drugs completely was next considered, and the speaker said that again and again cases had come to his notice where only one-half, three-fifths, two-thirds or three-fourths of these principles had been extracted from the drug operated upon. The foreman of the fluid-extract department of a large wholesale house was quoted as saying: "The manufacture of unassayed preparations and of standardized preparations are two different things. Before assaying was adopted, appearance was the only requirement, whether one-half or one-third of the active principles was extracted."

Then, summarizing his opinions, with reference to the foregoing statements, the speaker said: "In view of the variableness of the drugs, and the element of uncertainty introduced in manufacturing the various preparations, which is the most rational course to pursue: to make tinctures, varying in strength from a very small potency to the strength of fluid extracts, and fluid extracts, solid extracts, etc., varying in the same degree; or to make preparations that are uniform in strength?" In his mind there was only one answer. And again: "What tinctures, for example, will possess the greater degree of uniformity—those made from crude drugs varying extremely in potency, or those prepared from standardized fluid extracts, etc.?"

It was stated that, in preparing tinctures from their respective fluid extracts, the menstrua directed to be used were usually of such a strength that precipitation was obviated. In some cases, a small precipitate settled out on standing;

but this was also true of tinctures freshly prepared from the drug. If it was inert in one case, it remained to be demonstrated that it was not in the other.

The chairman, Mr. Joseph W. England, was opposed to the manufacture of other galenicals from fluid extracts, and referred to a paper prepared by him and published in the September, 1893, number of this JOURNAL, upon the question: "Is it possible to produce fluid extracts of such strength that they can be diluted with proper menstrua to standard tinctures?" Much of the argument then presented was brought forward by the speaker in support of his views on the subject proposed for discussion.

One of the statements which he emphasized was that different classes of proximate principles were yielded to menstrua of varying strength, and hence official tinctures could not be made from the respective fluid extracts, inasmuch as the menstrua for these two classes of preparations varied greatly in their proportions of alcohol and water as applied to different drugs, and in evidence of this, the menstrua for a number of these preparations were given in tabular form.

The claim was also made that an officially made tincture was relatively stronger than the corresponding fluid extract, the relatively larger dose of the fluid extract confirming this opinion.

The speaker stated that many manufacturers did not make their fluid extracts according to Pharmacopœial directions, but according to methods which their own experience suggested. Another point was the variation in menstrua which they used, which neither agreed with the Pharmacopœial requirements nor among themselves.

He, therefore, concluded that it was impossible to make tinctures uniform in strength from fluid extracts, whether these were assayed or not, inasmuch as the assay processes used likewise varied, as well as the standards assumed for many drugs.

Professor Remington said that the main question was in reference to the objects had in view concerning these two classes of preparations; that fluid extracts were intended to be permanent preparations and were made strongly alcoholic, while on the other hand, the menstrua for tinctures were made as aqueous as possible, and still extract and retain the desirable constituents of the drug.

He also said that some principles which could not be obtained with a small amount of dilute menstruum could be extracted from the drug by the use of a larger quantity of the solvent, whereas in the case of fluid extracts the object was to limit the quantity of menstruum.

In his opinion, to consider the question in reference to standardized fluid extracts was to limit it, as many manufacturers, who do not standardize these preparations, nevertheless give directions for diluting them in the preparation of tinctures.

The speaker remarked upon the custom among manufacturers of storing fluid extracts for a time and then removing the precipitates formed, and questioned the propriety of making tinctures from fluid extracts thus deprived of some of their constituents.

On motion, the meeting adjourned.

T. S. WIEGAND,
Registrar.